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Room temperature hydrogen detection using Pd-coated GaN nanowires

Wantae Lim,[1] J. S. Wright,[1] B. P. Gila,[1] Jason L. Johnson,[2] Ant Ural,[2] Travis Anderson,[3] F. Ren,[3] and S. J. Pearton[1,a)]

[1]*Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA*
[2]*Department of Electrical and Computer Engineering, University of Florida, Gainesville, Florida 32611, USA*
[3]*Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA*

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Multiple GaN nanowires produced by thermal chemical vapor deposition were employed as gas sensors for detection of hydrogen at concentrations from 200–1500 ppm in N_2 at 300 K. Palladium coating of the wires improved the sensitivity by a factor of up to 11 at low ppm concentrations relative to uncoated controls. The GaN nanowires showed relative responses of ~7.4% at 200 ppm and ~9.1% at 1500 ppm H_2 in N_2 after a 10 min exposure. Upon removal of hydrogen from the measurement ambient, ~90% of the initial GaN conductance was recovered within 2 min. Temperature dependent measurements showed a larger relative response and shorter response time at elevated temperature. The adsorption activation energy of the sensor was 2.2 kcal mol^{-1} at 3000 ppm H_2 in N_2. These sensors exhibit low power consumption (<0.6 mW) at 300 K. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975173]

There has been significant recent interest in the development of wide-band-gap semiconductor gas and chemical sensors, particularly for H_2 (Refs. 1–17) because of its use in fuel cells as an energy source to replace petroleum. Since H_2 is a hazardous, odorless, and highly flammable gas, H_2 gas sensors have attracted a great deal of attention, particularly for the detection of combustion gases for fuel leak detection in spacecraft, automobiles and aircraft, fire detectors, exhaust diagnosis, and emissions from industrial processes.[18–21] A key aspect of realizing these sensors is to selectively detect hydrogen with minimal power consumption near room temperature. Wide-band-gap semiconductors such as GaN and ZnO have excellent potential for H_2 gas sensing because of their sensitivity to surface charge and ability to operate over large temperature ranges.[9,22–24] Nanoscale materials in the form of nanowires, nanotubes, and nanoribbons are becoming promising candidates for H_2 gas sensors due to their high surface to volume ratio.[9,24–26] In addition, the use of metallic catalysts can functionalize the surface of nanomaterials by dissociating H_2 into atomic hydrogen. While H_2 sensors based on ZnO nanorods, SnO_2 nanowires, and In_2O_3 nanowires with excellent response and recovery characteristics have been reported in literature,[23,24,27] there have been few reports on H_2 gas sensors based on GaN nanowires, which should offer excellent environmental stability. In this letter, we report on the hydrogen sensing properties of Pd-coated multiple GaN nanowires at different hydrogen concentrations.

For GaN nanowire growth, we first prepared the growth substrate by *e*-beam evaporating gold of approximately 15 Å onto a clean piece of (100) Si with 100 nm of thermally grown oxide. Next, the Gallium metal source (99.999%) was poured into a quartz boat and placed into a tube furnace. We then inserted the growth substrate and positioned it within 3 cm downstream of the Ga metal source. The growth chamber was purged with Ar for 10 min at room temperature to remove any residual oxygen. The substrate was heated up to 850 °C and annealed for 15 min under Ar ambient. This annealing is required for the successful formation of Au catalyst nanoparticles on the sample surface. After the annealing step, high purity NH_3 (99.999%) and H_2 (99.999%) were introduced into the growth chamber. The GaN nanowires were grown for ~5 h at 850 °C. Finally, the sample was removed from the chamber when its temperature dropped below 100 °C to prevent the oxidation of the nanowires. The typical length of the resultant GaN nanowires was 5–10 μm. X-ray diffraction, high resolution transmission electron micrscopy, and photoluminescence showed the nanowires to be single-crystal wurtzite GaN.

Figure 1 shows scanning electron microscopy (SEM) micrographs of as-grown nanowires. A layer of 10-nm-thick Pd was deposited by sputtering onto the nanowires to verify the effect of catalyst on gas sensitivity. For the Ohmic contacts, Ti(20 nm)/Al(80 nm)/Pt(40 nm)/Au(80 nm) were deposited by *e*-beam evaporator and patterned by photolithography and lift-off process to form two contact pads on multiple nanowires. The contacts were annealed at 350 °C for 60 s in flowing N_2 ambient in a rapid thermal annealing furnace. Au wires were bonded to the contact pads for device packaging. The device was exposed to different H_2 concentrations (200–3000 ppm H_2 in N_2) ambient in an environmental chamber at 25–150 °C. The current-voltage (*I-V*)

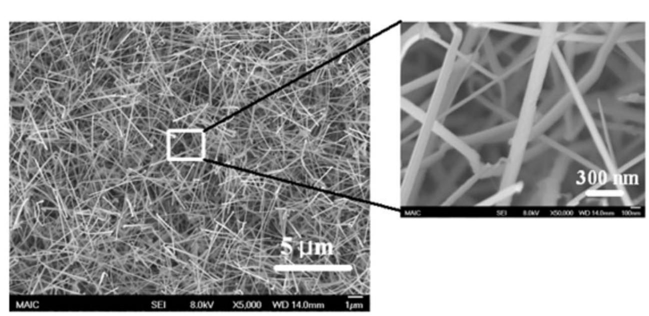

FIG. 1. SEM images of as-grown GaN nanowires.

a)Electronic mail: spear@mse.ufl.edu.

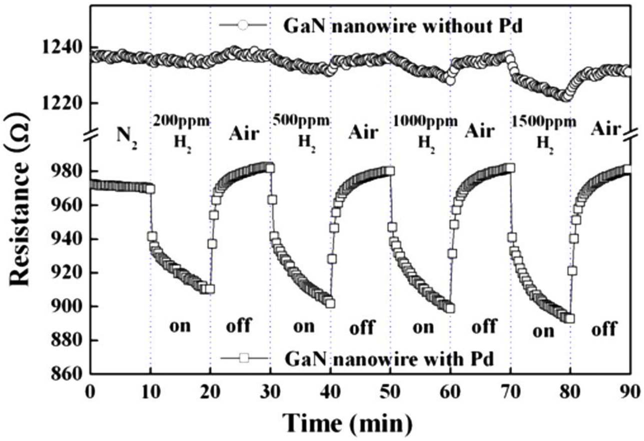

FIG. 2. (Color online) Measured resistance at an applied bias of 0.5 V as a function of time from Pd-coated and uncoated multiple GaN nanowires exposed to a series of H_2 concentrations (200–1500 ppm) in N_2 for 10 min at room temperature.

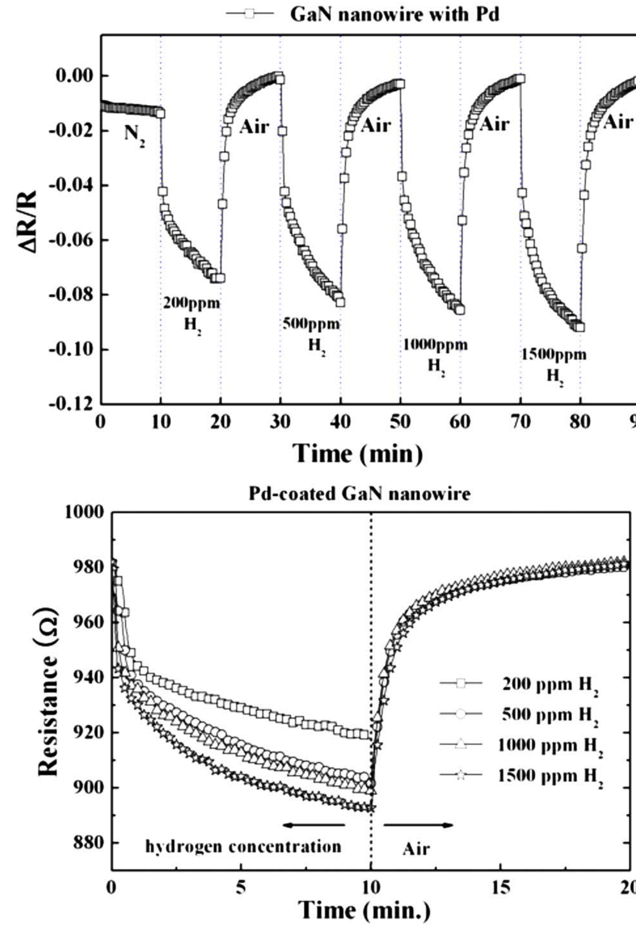

FIG. 3. (Color online) Relative response of Pd-coated GaN nanowires at different hydrogen concentrations (top) and time dependent resistance change of Pd-coated multiple GaN nanowires at different hydrogen concentrations (bottom).

characteristics from multiple nanowires were linear with a maximum power consumption of <0.6 mW under our operating conditions.

Figure 2 shows the measured resistance at a bias of 0.5 V as a function of time from Pd-coated and uncoated multiple GaN nanowires exposed to a series of H_2 concentrations (200–1500 ppm) in N_2 for 10 min at room temperature. Pd coating of the nanowires improved the sensitivity to ppm level H_2 by a factor of up to 11. The addition of Pd appears to be effective in catalytic dissociation of molecular hydrogen. Diffusion of atomic hydrogen to the metal/GaN interface alters the surface depletion of the wires and hence the resistance at fixed bias voltage.[9] The resistance change depended on the gas concentration but the variations were small at H_2 concentration above 1000 ppm. The resistance after exposing the nanowires to air was restored to approximately 90% of initial level within 2 min.

Wang *et al.*[24] reported that Pd-uncoated multiple ZnO nanorods had relative resistance change of $\sim$0.25% for 500 ppm H_2 in N_2 after a 10 min exposure at room temperature. However, Pd-coated ZnO nanorods showed a high sensitivity ($>$4.2%) and fast response at the same H_2 concentration. By comparison, Pd-coated GaN nanowires presented relative responses of $\sim$7.4% at 200 ppm, $\sim$8.2% at 500 ppm, and $\sim$9.1% at 1500 ppm H_2 in N_2, as shown in Fig. 3 (top). Moreover, the relative responses of uncoated nanowires were $\sim$0.48%, 0.57%, and 1.2%, respectively, under the same conditions, i.e., the GaN nanowire sensors are more sensitive to hydrogen than ZnO nanorod sensors under the conditions used here. The maximum power consumption during the measurement was <0.6 mW. This is suitable for long-term hydrogen sensing applications. Figure 3 (bottom) shows the time dependent resistance change in Pd-coated multiple GaN nanowires as the gas ambient is switched from air to various concentrations of H_2 in N_2 (200–1500 ppm) and then back to air. The rate of resistance change was sharply increased and then reached maximum at the exposure time of 1 min, which might be due to the Pd being covered with native oxide. As the native oxide was removed by H_2 exposure, the rate increased with time. However, the rate decreased after 1 min because the Pd surface was gradually saturated with H_2 and limited in supply of atomic hydrogen to the Pd/nanowire interface. The resistance of the nanowires was changed back to their initial values after switching from H_2 to air. The recovery of resistance is most likely dominated by the removal of hydrogen atoms from the Pd/nanowire interface.[5,9,24] Such gas detection mechanism is attributed to the change in atomic hydrogen concentration at the interface upon H_2 and air exposure, causing change in resistance.[9,28]

The temperature dependence of resistance from Pd-coated multiple GaN nanowires exposed to 3000 ppm H_2 in N_2 is shown in the Fig. 4. The relative response saturated above a measurement temperature of $\sim$100 °C, which could be due to the limitation in supply of atomic hydrogen as we discussed in Fig. 3. The rate of resistance change dramatically increased with time at 150 °C and was a factor of about 5 faster than that at room temperature. The inset figure shows the Arrhenius plot of rate of nanowire resistance change. An adsorption activation energy of 2.2 kcal mol^{-1} was estimated from the standard Arrhenius equation. This value is smaller than that of multiple ZnO nanorods, confirming the higher sensitivity and faster response of the GaN nanowire sensor.

In conclusion, Pd-coated GaN nanowires appear well suited to detection of ppm concentration of hydrogen at room temperature. Pd-coated nanowires showed an improvement in the sensitivity by up to a factor of 11 larger than uncoated controls. The results indicate that Pd-coated GaN nanowires are promising for hydrogen gas sensors with fast response,

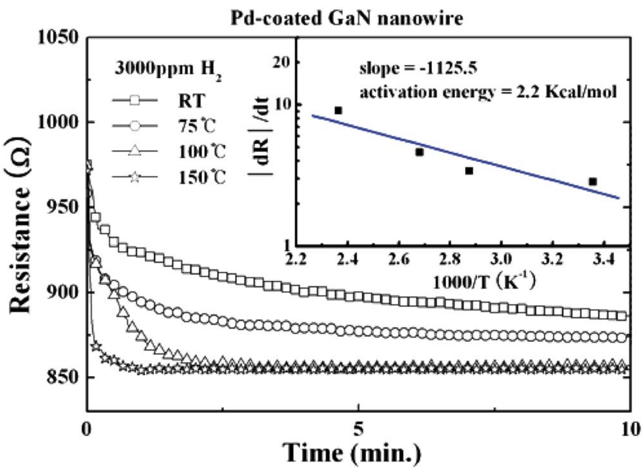

FIG. 4. (Color online) Temperature dependence of resistance from Pd-coated multiple GaN nanowires exposed to 3000 ppm H_2 in N_2 (the inset figure shows the Arrhenius plot of rate of resistance change for the highest change in resistance, i.e., from 1–20 s).

high sensitivity, and low power consumption at low temperature.

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