Hydrogen sensing with Pt-functionalized GaN nanowires

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Pt-coatings sputtered on to multiple GaN nanowires is shown to enhance their sensitivity for hydrogen at the hundreds of ppm level at 25 °C. GaN nanowires without a metal coating showed no detectable change in current when exposed to hydrogen under the same conditions. Pt-coated multiple GaN nanowires gave non-linear relative responses of ~1.7% at 200 ppm up to ~1.9% at 2000 ppm H2 in N2 after a 10-min exposure. More than 80% of the initial GaN conductance was recovered within 2 min after removal of hydrogen from the measurement medium. At higher temperatures, larger resistance changes and faster response and recovery were obtained. The adsorption activation energy of the sensor was 7.3 kcal mol−1 at 2000 ppm H2 in N2. Pt-coated GaN nanowire sensors resulted in much lower relative response than Pd-coated sensors.

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Continued research into the use of H2 as an energy source has necessitated the development of robust, low power hydrogen-selective gas sensors [1–4]. Because H2 is a hazardous, odorless, and flammable gas, H2 gas sensors have many possible niche uses, particularly for combustion gas detection for fuel leak detection in spacecraft, autos and aircraft, fire detectors, and industrial process emissions [5–8]. Central to realizing these next-generational sensors is the ability to detect hydrogen with minimal power consumption at or much below room temperature. Wide bandgap semiconductors such as GaN and ZnO are possible popular materials for H2 gas sensing in part to their sensitivity to surface charge and wide temperature stability [9–19]. One-dimensional (1-D) nanomaterials (nanowires, nanotubes, nanorods, and nanobelts) show increasing potential as H2 gas sensors due to their high surface to volume ratio [20–29]. Numerous groups have already reported the use of H2 sensors based on carbon nanotubes (CNTs) [23], ZnO nanorods [12], and SnO2 nanowires [23] with excellent response and recovery characteristics, although there are few studies on H2 gas sensors based on GaN nanowires, which may offer excellent environmental stability.

Critical to the functionalization of nanomaterial H2 sensors is the addition of a thin metallic catalytic coating. While the mechanism of this functional layer for H2 sensing is well understood, the choice of material still seems a matter of preference. Although both Pt and Pd have typically been accepted as choice metals for functional layers on oxide- and nitride-based sensors in numerous reports, there have been few studies to compare Pt and Pd metal functionalities. In this letter, we evaluate the hydrogen sensing properties of Pt-coated multiple GaN nanowires at different hydrogen concentrations and compare to previous results from similar Pd-coated multiple GaN nanowire sensors.

For GaN nanowire growth, a growth substrate was prepared by e-beam evaporating 15 Å gold onto a clean piece of (1 0 0) Si with 100 nm thermally grown oxide. A Gallium metal source (99.999%) was poured into a quartz boat and placed into a tube furnace. The growth substrate was positioned within 3 cm downstream of the growth substrate and heated up to 850 °C to prevent oxidation. The growth substrate was positioned 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 in an Ar ambience to allow for the formation of Au catalyst nanoparticles on the sample surface. After annealing, high purity NH3 (99.999%) and H2 (99.999%) were introduced for growth. The GaN nanowires were grown for ∼3 h at 850 °C. Nanowire samples were removed after the temperature cooled to below 100 °C to prevent oxidation. Typical length of the resultant GaN nanowires was 2–6 µm. X-ray diffraction, high-resolution transmission electron microscopy, and photoluminescence showed the nanowires to be single-crystal wurtzite GaN.

A shadow mask was used to pattern non-alloyed rf-sputtered Ti (50 nm)/Al (80 nm)/Pt (40 nm)/Au (300 nm) Ohmic contacts on the GaN nanowires with a contact separation of ∼50 µm. Au wires were bonded to the contact pads for device packaging. Finally, a ∼7-nm-thick functional layer of Pt was sputter-deposited onto the nanowire device. The GaN nanowire sensors were exposed to different H2 concentrations (200–2000 ppm H2 in N2 ambience) at 25–100 °C. Sensor response was compared to previous results for...
Pd-coated GaN nanowire H2 sensors [30]. Fig. 1 shows scanning electron micrographs (SEMs) of the nanowires with the added Pt-coating. The current–voltage (I–V) characteristics from multiple nanowires were linear with a maximum power consumption of <0.3 mW under our operating conditions.

Measured resistance at a bias of 0.1 V as a function of time is shown in Fig. 2 (top) for Pt-coated multiple GaN nanowires exposed to varying H2 concentrations (200–2000 ppm) in N2 for 10 min at room temperature. The measured resistance for uncoated multiple GaN nanowires exposed to 2000 ppm H2 concentration is shown for comparison. The addition of the functional Pt-coating is critical to H2 detection for these sensors. Specifically, it is believed Pt works to catalytically dissociate molecular H2 into atomic hydrogen. Diffusion of atomic hydrogen to the metal/GaN interface alters the surface charge by depletion and induces a current response at a fixed bias [9].

Current response is nearly instantaneous upon exposure to H2. Although it takes >5 min for hydrogen to saturate the relative response, initial resistance change is noted in less than 2 s from H2 exposure (minimum increment of measurement). Similar Pd-coated GaN nanowire H2 sensors also exhibited instantaneous changes in resistance upon H2 exposure. The diffusion of hydrogen through the Pt-coating is not the limiting factor in the time response of the sensor, but rather the mass transport of gas into the enclosure as we have observed by altering the H2 introduction rate (not shown). Resistance change depends on the gas concentration and recovers to 80% of the initial level within 2 min. Resistance recovery is probably controlled by the removal of hydrogen atoms from the Pt/nanowire interface [12].

The rate of resistance change of GaN nanowire sensors upon exposure to H2 is time dependent. Resistance decreases slowly in the first minute after H2 exposure, likely due to the Pt functional layer being covered with native oxide. As the native oxide was removed with continued H2 exposure, the rate increased with time. However, after ~2 min the rate decreased as the Pt surface became gradually saturated with H2 and limited the supply of atomic hydrogen to the Pt/nanowire interface.

Previously, we reported that Pd-coated multiple GaN nanowires showed high sensitivity to low H2 concentrations (~7.4% at 200 ppm) [30]. Uncoated nanowire sensors displayed little to no response at similar concentrations of H2. By comparison, Pt-coated GaN nanowires gave relative responses of ~1.7% at 200 ppm, ~1.8% at 1200 ppm, and ~1.9% at 2000 ppm H2 in N2. As the maximum power consumption in either case is <0.6 mW, both Pt and Pd functionalized GaN nanowire sensors are suitable for long-term hydrogen sensing applications. Fig. 2 (bottom) shows the time dependent relative response of Pt-coated multiple GaN nanowires at varying concentrations of H2 in N2 ambience. Pt-coated GaN nanowire sensors are less sensitive to hydrogen than the same nanowires with a Pd coating. Pd coatings have also shown to have higher sensitivity than similar Pt layers for multiple InN nanobelt H2 sensors. This is in contrast to results for ZnO nanowire H2 sensors.

![Fig. 1. SEM images of GaN nanowires after Pt-coating.](image1)

![Fig. 2. Measured resistance at an applied bias of 0.1 V as a function of time from Pt-coated and uncoated multiple GaN nanowires exposed to varying H2 concentrations (200–2000 ppm) in N2 ambience for 10 min at room temperature (top), and the time dependent relative response of Pt-coated GaN nanowires at different H2 concentration (bottom).](image2)
The relative response for Pt-coated GaN nanowires exposed to 1000 ppm H₂ in N₂ at a fixed bias of 0.1 V for 10 min measured over a temperature range (25–100 °C) is shown in Fig. 3. Relative response increased with measurement temperature from 1.8% at room temperature up to 4% at 100 °C, resulting from the increase in catalytic dissociation rate of molecular hydrogen (H₂) or diffusion rate of atomic hydrogen into the Pt/GaN interface. This response is at least 50% smaller for all temperatures in comparison to similar Pd-coated GaN nanowires. An extrapolation of the trend line suggests there would still be at least a 1.5% relative change in current at temperatures as low as 0 °C. This result is supportive of the viability of GaN nanowire H₂ sensors for low temperature applications.

An Arrhenius plot of rate of nanowire resistance change was used to calculate an adsorption activation energy of 7.3 kcal mol⁻¹, shown in Fig. 4. The rate of resistance change taken for the Arrhenius plot was from the first 20 s of H₂ exposure at each respective temperature. This initial exposure coincides with the highest rate of resistance change through the GaN nanowire sensors and is representative of the chemiadsorption of H to the nanowire/metal interface [12]. This value is larger than that of similar previous Pd-coated multiple GaN nanowires (2.2 kcal mol⁻¹) [30], which could be indicative of the lower sensitivity and slower response of the Pt functional layer. Although both sensors featured contact separations of 50 µm and used sputter-deposited metal coatings, the thickness of the Pd coating was ~10 nm while the thickness of the Pt-coating was only ~7 nm. Additionally, though the GaN nanowire samples for both studies were grown in the same fashion, the baseline resistance of the GaN nanowire samples used in the Pd-coated study was ~1240 Ω where as the baseline resistance for samples used in this study was only 53 Ω. This difference in resistance is representative of the large differences in nanomaterial quality that occur even for samples grown under identical conditions and could be resultant from a higher percentage of oxide growth from one sample as compared to the other. An accurate comparison between metal coated sensors will demand GaN nanowire samples grown from the same substrate and must have identical coating thicknesses; such an investigation is on-going.

Regardless of the difference between Pt/Ga and Pd coated sensors, the difference between Pt and Pd coated nanomaterial sensor activation energy has been noticed before for multiple InN nanobelts although the opposite has been shown for multiple ZnO nanowires. This is suggestive of a material difference at the (Pd/Pt)/nanowire interface between nitride- and oxide-based nanoscale sensors and will need more data to be understood.

The inset figure displays the temperature dependence of resistance from 1000 ppm H₂ exposure. The rate of resistance change is drastically increased with increasing temperature. Resistance change is a factor of about 10 faster at 100 °C than that at room temperature. This is supportive of an increase in atomic hydrogen reaching the Pt/GaN interface with increasing temperature.

In conclusion, Pt-coated multiple GaN nanowires operated at low bias (0.1 V) are not as effective as sensors for detection of ppm hydrogen at room temperature as similar Pd-coated nanowire sensors. Pt-coated nanowires showed a marked decrease in sensitivity by a factor of up to 50% than Pd-coated sensors, explained by higher activation energy. However Pt-coated nanowire sensors did show significant response to hydrogen in comparison to uncoated controls. The results suggest Pd-coated GaN nanowires may be more suitable as hydrogen gas sensors than Pt-coated nanowires.

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References


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