Virginia Commonwealth University
VCU Scholars Compass

Electrical and Computer Engineering Publications | Dept. of Electrical and Computer Engineering

2005

GaN resistive hydrogen gas sensors

Feng Yun
Virginia Commonwealth University, fyun@vcu.edu

Serguei A. Chevtchenko
Virginia Commonwealth University, chevtchenkos@vcu.edu

Yong-Tae Moon
Virginia Commonwealth University

See next page for additional authors

Follow this and additional works at: http://scholarscompass.vcu.edu/egre_pubs

Part of the Electrical and Computer Engineering Commons

Yun, F., Chevtchenko, S., Moon, Y.-T., et al. GaN resistive hydrogen gas sensors. Applied Physics Letters, 87, 073507 (2005). Copyright © 2005 AIP Publishing LLC.

Downloaded from

http://scholarscompass.vcu.edu/egre_pubs/121

This Article is brought to you for free and open access by the Dept. of Electrical and Computer Engineering at VCU Scholars Compass. It has been accepted for inclusion in Electrical and Computer Engineering Publications by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.

Authors
Feng Yun, Serguei A. Chevtchenko, Yong-Tae Moon, Hadis Morkoç, Timothy J. Fawcett, and John T. Wolan

This article is available at VCU Scholars Compass: http://scholarscompass.vcu.edu/egre_pubs/121

HTML ABSTRACT + LINKS

GaN resistive hydrogen gas sensors

Feng Yun,[a] Serguei Chevtchenko, Yong-Tae Moon, and Hadis Morkoç
Department of Electrical and Computer Engineering and Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284

Timothy J. Fawcett and John T. Wolan
Chemical Engineering Department, University of South Florida, Tampa, Florida 33620

(Received 19 April 2005; accepted 29 June 2005; published online 10 August 2005)

GaN epilayers grown by organometallic vapor phase epitaxy have been used to fabricate resistive gas sensors with a pair of planar ohmic contacts. Detectible sensitivity to H_2 gas for a wide range of gas mixtures in an Ar ambient has been realized; the lowest concentration tested is ~0.1% H_2 (in Ar), well below the lower combustion limit in air. No saturation of the signal is observed up to 100% H_2 flow. Real-time response to H_2 shows a clear and sharp response with no memory effects during the ramping cycles of H_2 concentration. The change in current at a fixed voltage to hydrogen was found to change with sensor geometry. This appears to be consistent with a surface-adsorption-induced change of conductivity; a detailed picture of the gas sensing mechanism requires further systematic studies. © *2005 American Institute of Physics*.
[DOI: 10.1063/1.2031930]

There is a considerable interest in developing gas sensors capable of operation in harsh environmental conditions such as high-temperature and chemically corrosive ambients. Due to the large band gap of GaN and SiC, and the associated chemical stability and mechanical robustness, these semiconductors can be used for many harsh applications. These include gas sensing operations during chemical reactor processing, onboard fire alarms on aircraft and space vehicles, as well as detection of fuel leaks in automobiles and aircraft, to name a few.[1–3] A unique advantage of a GaN gas sensor is that it can be integrated with GaN-based solar-blind UV photodetectors or high-power, high-temperature electronics devices on the same chip. Recently, there have been reports on GaN gas sensors utilizing Schottky contacts,[4–7] where a catalytic metal such as Pt or Pd facilitates the adsorption of hydrogen atoms on the semiconductor surface to form a polarized layer. This layer shifts the electrostatic potential, which in turn changes the work function of the metal and, therefore, the effective Schottky barrier height. Such types of devices have detection ranges typically below the combustion point (~4.7% H_2 in air) of hydrogen. Resistive gas sensors, on the other hand, do not rely on the requisite quality of Schottky contacts and the specific catalytic metals for gas detection. Instead, they exploit the change in the near surface conductivity most likely due to the adsorption of gas species. Historically, most of the resistive gas sensors studied that employ a change of surface conductivity have been metal-oxide semiconductors such as ZnO,[8] SnO2,[9] In_2O_3,[10] MoO_3,[11] WO_3,[12] and titanium-substituted chromium oxide[13] (CTO). In the case of oxygen-containing gases, oxygen is believed to adsorb on the semiconductor surface and create an electron acceptor state within the band gap of *p*-type semiconductors, whereas the reducing gases such as H_2 create an electron donor state in *n*-type semiconductors.[14] Thus the surface adsorption results in a change in the fractional surface coverage of this acceptor/donor state and hence a change in conductivity that can be detected as the response.

Recently, Fawcett *et al.*[15] reported on a resistive hydrogen gas sensor based on the change in the surface conductivity of 3C–SiC epilayers. The sensor was able to detect hydrogen in a wide range (0.33–100 %) with no sign of saturation or hysteresis effects. To our knowledge, there has been no report on resistive hydrogen gas sensors made from GaN to date. It is of interest to study the resistive GaN gas sensor due to its simplicity, reliability, and unique potential applications. It is also of significant scientific merit to understand the gas sensing mechanism for this type of GaN sensor. In this letter, we report on the fabrication of GaN resistive gas sensors and preliminary results of these devices as hydrogen gas sensors.

The GaN resistive gas sensors were fabricated using a Si-doped GaN epilayer (2 μm in thickness) grown by organometallic vapor phase epitaxy (OMVPE), on *c*-plane sapphire substrates. The GaN film exhibited an *n*-type carrier concentration of $\sim 1\times 10^{18}$ cm^{-3} at room-temperature. For resistive sensor fabrication, a stack of Ti(300 Å)/Al(1000 Å)/Ti(300 Å)/Au(300 Å) planar ohmic contact metallization was deposited by *e* beam (for Ti) and thermal evaporation (for Al and Au), followed by rapid thermal annealing at 900 °C for 60 s in N_2 ambient. After depositing a Au overlay (~1500 Å) on the contact pads, contact electrodes were wire bonded to a carrier for testing. Two devices were fabricated with the same ohmic contact dimensions of 1 mm × 3 mm, which span an area of 3 mm^2, with different gaps of 0.5 mm (exposed active area=1.5 mm^2) and 1.0 mm (exposed active area=3.0 mm^2) between the contacts. Both devices showed ideal ohmic characteristics with resistances of ~25 Ω (for the 1.5-cm^2 sample) and ~46 Ω (for the 3.0-mm^2 sample). Both devices were then contacted to by Ni wires secured to the Au contact leads from a ceramic carrier via stainless steel screws and simultaneously loaded into a quartz tube for testing with various gas flows.

The sensor response to hydrogen flow was recorded as the change of current (ΔI) passing between the planar contacts for a constant applied dc voltage of 2 V. The reference

[a]Author to whom correspondence should be addressed; electronic mail: fyun@vcu.edu

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.172.48.59 On: Wed, 15 Apr 2015 16:07:57

 © 2005 American Institute of Physics

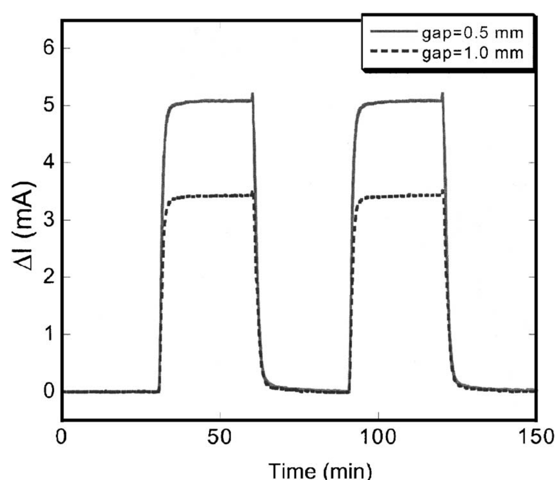

FIG. 1. Change in current at a fixed dc voltage of 2 V to pure H_2 pulses at 50 °C, purged by Ar gas in between the cycles for both GaN sensors with gaps of 1.0 mm (dashed line) and 0.5 mm (solid line).

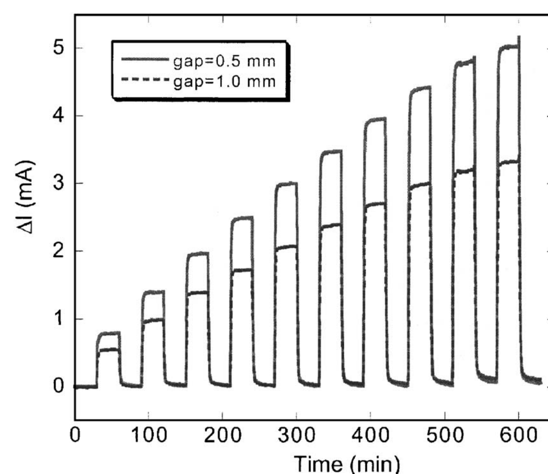

FIG. 2. Change in current at a fixed dc voltage of 2 V to H_2 at 50 °C, at various concentrations from 10% to 100% diluted in Ar, with Ar gas purge in between the cycles, for both GaN resistive gas sensors with gaps of 1.0 mm (dashed line) and 0.5 mm (solid line).

point is at 0% H_2 in an Ar ambient flow. Figure 1 shows the evolution of the differential current as the sensors were exposed to pure hydrogen at 50 °C, cycled with an Ar gas purge in between the H_2 flow steps. Several features can be observed in Fig. 1. First, the response to H_2 is very reproducible both at maximum H_2 flow and at no H_2 flow for many cycles. Second, the ramp-up response time is ≤7 min following the onset of the H_2 flow. The ramp-down response time is ≤10 min following the switch from H_2 to Ar gas. Compared to the reported SiC resistive sensors with the same geometry,[15] the response of the GaN sensors is approximately twice as fast for 100% steady-state response. The time for first response is approximately 2 s and 30 s for the SiC and GaN devices, respectively. Finally, the response for the 0.5-mm-gap device is found to be ~1.5 times larger than that for the 1.0-mm-gap device.

Figure 2 shows the sensor response to different concentrations of H_2 at 50 °C, with an Ar gas purge in between the H_2 cycles. The hydrogen gas was diluted in Ar with concentrations ranging from 10% to 100% (pure H_2), in 10% steps. For both sensors with 0.5- and 1.0-mm gaps, the current response is almost linear with H_2 concentration within the tested range, and there is no sign of saturation even for pure hydrogen. The sensors did not show memory effects caused by residual hydrogen adsorption on the sensor surface after each Ar purge cycle, as evidenced from the clear drop back to zero after each Ar purge. For the 0.5-mm-gap sensor, the response is higher than that of the 1.0-mm-gap sensor, by a factor of ~1.5, consistent with the observation in Fig. 1.

As the H_2 concentration was diluted further, the GaN resistive gas sensors remained operative. Shown in Fig. 3 are the current responses to low concentrations of H_2 at 50 °C. The H_2 concentration was varied from 4.7% (in Ar), in a decrement of 0.5%, down to 0.5%. For both devices with gaps of 1.0 and 0.5 mm, the small variation of 0.5% H_2 concentration can be clearly differentiated. In particular, for the 0.5-mm-gap sensor, a linear relationship between the current response and H_2 flow was maintained between 0.5% and 4.7% of H_2. In fact, Fig. 3 shows that the lower detection limit has been reduced to 0.1% H_2 for both devices. Unlike the Si hydrogen sensors based on a similar geometry, which saturate above ~40% of H_2 concentration,[15] the GaN resistive sensors remain highly sensitive throughout the entire range of 0.1% to 100% of H_2 in Ar, with a linear response.

In the field, many applications require a hydrogen sensor to function reliably in a continually varying H_2 environment with no purge cycle in between the changing H_2 concentrations. This scenario was simulated in Fig. 4, where the current response of the GaN resistive sensors was recorded under continuous flow of H_2 gas with concentrations varying from 10% to 100%, at 10% increments, without an Ar purge in between at 50 °C. It is remarkable that very clear plateau responses for both the 0.5- and the 1.0-mm-gap sensors have been demonstrated. Again, the ratio of the responses for the 0.5- to the 1.0-mm-gap sensors is ~1.5. The sensor response is reproduced consistently and repeatedly for both geometries during the ramp-up and ramp-down stages of the H_2 concentration, making them very reliable candidates for wide-range H_2 sensors. There is no indication of any saturation, memory effects, or deformation of response in this continuous operation mode.

The gas sensing mechanisms for the GaN resistive sensors discussed here are different from those widely accepted for GaN sensors adopting Schottky and metal-insulator-semiconductor (MIS) structures where the creation of a po-

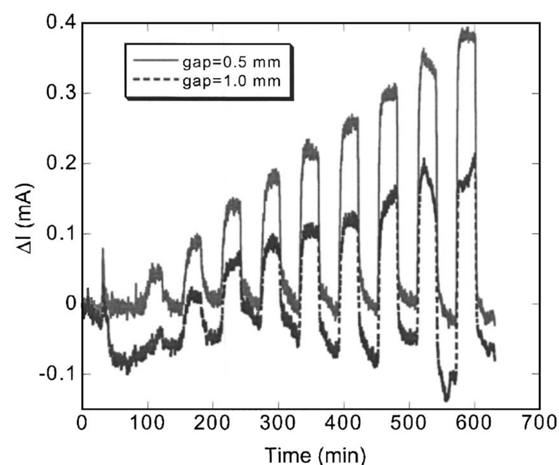

FIG. 3. Change in current at a fixed dc voltage of 2 V to a low concentration of H_2 at 50 °C, from 0.1% to 4.7% of H_2 diluted in Ar, with Ar gas purge in between the cycles, for both GaN resistive gas sensors with gaps of 1.0 mm (dashed line) and 0.5 mm (solid line).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.172.48.59 On: Wed, 15 Apr 2015 16:07:57

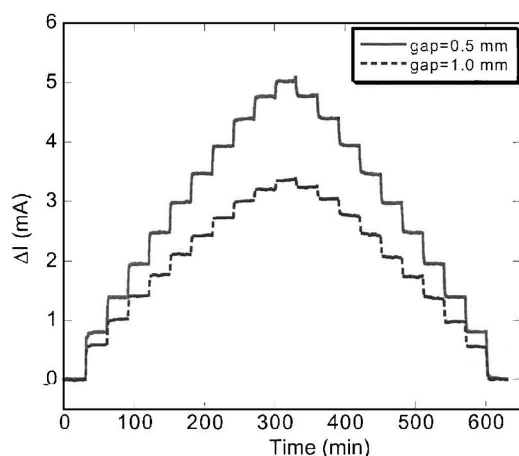

FIG. 4. Change in current at a fixed dc voltage of 2 V to H_2 at 50 °C, under continuous operation mode (without the Ar purge between cycles), at various concentrations from 10% to 100%, and then from 100% to 10% of H_2 diluted in Ar, for both GaN resistive gas sensors with gaps of 1.0 mm (dashed line) and 0.5 mm (solid line).

larized layer near the metal/GaN interface by H atoms assisted by the diffusion through the catalytic metal and resultant change in the work function form the genesis of operation.[4,5] In the GaN resistive sensors discussed here, the devices are free from Pt or Pd, and are covered with a thick layer of Au, which is regarded as an inhibitor to H adsorption and diffusion.[16] Thus, the effects of H adsorption and diffusion in the devices under discussion being associated with any catalytic metal-related effects can be ruled out.

A plausible explanation is the surface adsorption of H species leading to the reduction in surface resistance in a fashion similar to the oxide-based sensors.[12] If this assumption is true, the ratio of the change of surface resistance to the total resistance would be roughly inversely proportional to the gap between the electrodes, resulting in a reduced current response with increased gap between the electrodes. This is indeed the case for the GaN resistive sensors reported here. For the GaN sensor with a 1.0-mm gap, the current response decreases by ~1.5 times compared to that with a 0.5-mm gap, consistent for all the measurements described above. Our experimental data on GaN sensors strongly indicate that surface adsorption is a likely gas sensing mechanism for the observed current response of the GaN resistive sensors.

To shed more light on the role of H on GaN surfaces, we have simulated a case of a H-passivated surface by dipping the same GaN wafer used for sensor fabrication in diluted HF solution that is known to passivate dangling bonds. The change in the surface band bending was measured by the surface potential method using electric force microscopy[17] (EFM) with reference potential to the Au contact pads. An increase of 0.2(±0.1) V in surface potential was recorded after the HF treatment, which corresponds to a decrease of band bending by 0.2(±0.1) V. As a consequence, the conductivity near the surface is increased. Although the chemical reactions for HF treatment and H_2 gas sensing are not identical, the H-treated GaN surface shows enhanced conductivity consistent with the H-sensor response data presented above.

For completeness, it should be mentioned that Ga-polar (0001) surfaces of GaN have been theoretically predicted to be energetically unfavorable for hydrogen as compared to the N-polar (000$\underline{1}$) surfaces where the hydrogen has very high affinity.[18] Another theoretical work pointed out[19] that H^- (not H^+) is stable in *n*-type GaN, making the incorporation of hydrogen to counteract rather than increase the conductivity in GaN due to dopant passivation. A more detailed ongoing study including the geometrical dependence, temperature behavior, and the doping effects on GaN hydrogen sensors may elucidate the effects of hydrogen on the electrical properties of GaN and the hydrogen sensing mechanisms.

In summary, GaN resistive hydrogen gas sensors have been fabricated and tested. A wide-range hydrogen sensing capability, from 0.1% to 100% of H_2 in Ar gas, has been demonstrated. The response, as measured by the change in current at a constant dc voltage of 2 V, is linear with respect to the H_2 content in Ar gas, and there is no saturation in the response even for pure H_2. In the continuous mode of operation, the GaN resistive sensors exhibited clear plateaus with a sharp reproducible response, without any memory effects during the ramp-up and ramp-down cycles. The experimental data are consistent with the premise that the likely gas sensing mechanism is surface adsorption and the associated change in the surface conductivity of GaN.

The authors are grateful to Professor J. Puru, Dr. Q. Sun, Dr. Q. Wang, and Dr. K. Zhu, for helpful discussions, and Dr. S. Dogan for assistance in wire bonding. This work is funded by ONR as part of a DURINT program and monitored by Dr. C. E. C. Wood of ONR.

[1]S. C. Pyke and L. Sadwick, Proceedings of the 2001 DOE Hydrogen Program Review, NREL/CP-570-30535, Baltimore, MD, 2001 (unpublished).
[2]A. Lloyd Spetz, A. Baranzahi, P. Tobias, and I. Lundstrom, Phys. Status Solidi A **162**, 493 (1997).
[3]B. P. Luther, S. D. Wolter, and S. E. Mohnley, Sens. Actuators B **56**, 164 (1999).
[4]J. Schalwig, G. Muller, L. Gorgens, and G. Dollinger, Appl. Phys. Lett. **80**, 1222 (2002).
[5]Jihyan Kim, F. Ren, B. P. Gila, C. R. Abernathy, and S. J. Pearton, Appl. Phys. Lett. **82**, 739 (2003).
[6]Jihyun Kim, B. P. Gila, C. R. Abernathy, G. Y. Chung, F. Ren, and S. J. Pearton, Solid-State Electron. **47**, 1487 (2003).
[7]O. Weidemann, M. Hermann, G. Steinhoff, H. Wingbrant, A. Lloyd Spetz, M. Stutzmann, and M. Eickhoff, Appl. Phys. Lett. **83**, 773 (2003).
[8]T. Seiyama, A. Kato, K. Fulishi, and M. Nagatani, Anal. Chem. **34**, 1502 (1962).
[9]A. Chiba, *Chemical Sensor Technology*, edited by S. Yamauchi (Kodansha, Tokyo, 1991), Vol. 4, p. 1.
[10]T. Takada, K. Suzuki, M. Nakane, Sens. Actuators B **13**, 404 (1993).
[11]A. Gurlo, N. Barsan, M. Ivanovskaya, U. Weimar, and W. Gopel, Sens. Actuators B **47**, 92 (1998).
[12]D. E. Williams, Sens. Actuators B **57**, 1 (1999).
[13]G. S. Henshaw, D. H. Dawson, and D. E. Williams, J. Mater. Chem. **5**, 1791 (1995).
[14]H. Windischmann and P. Mark, J. Electrochem. Soc. **126**, 627 (1979).
[15]T. J. Fawcett, J. T. Wolan, R. L. Myers, J. Walker, and S. E. Saddow, Appl. Phys. Lett. **85**, 416 (2004).
[16]E. Souteyrand, D. Nicolas, and J. R. Martin, Sens. Actuators B **24**, 871 (1995).
[17]S. Sabuktagin, M. A. Reshchikov, D. K. Johnstone, and H. Morkoç, Mater. Res. Soc. Symp. Proc. **798**, Y5.39 (2004).
[18]J. E. Northrup and J. Neugebauer, Appl. Phys. Lett. **85**, 3429 (2004).
[19]Chris G. Van de Walle and J. Neugebauer, Nature (London) **423**, 626 (2003).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.172.48.59 On: Wed, 15 Apr 2015 16:07:57