GaN Resistive Gas Sensors for Hydrogen Detection

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Abstract. We report on the fabrication and testing of GaN resistive gas sensors for hydrogen detection. The Si-doped n-type GaN was grown by organometalic vapor phase epitaxy (OMVPE) on *c*-plane sapphire substrates. The device structure is simply a pair of metal ohmic contact pads. The sensors are sensitive to H_2 gas over a wide range of concentration: the lowest concentration tested being ~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. In the continuous operation mode with varying H_2 concentration, a clear and sharp response was recorded with no memory effects during ramping up and down cycles of H_2 concentration. The change in current at a fixed voltage to hydrogen was found to change with sensor geometry. The possible gas sensing mechanisms are still under investigation.

Introduction

Gas sensors capable of operation in harsh environmental conditions such as high temperature and chemically corrosive ambients are highly desirable. The large bandgap of GaN and SiC allow high temperature operation with chemical stability and mechanical robustness [1,2]. In addition, GaN gas sensors have the unique advantage of integration with GaN-based solar-blind UV photodetectors or high power, high temperature electronics units on the same chip. So far, most of the reported GaN gas sensors utilize Schottky contacts [2,3,4,5,6] made of catalytic metals such as Pt or Pd, and measure the change of effective Schottky barrier height due to H_2 adsorption. The detection limit typically is below the combustion point (~4.7% H_2 in air). In this paper, we present GaN resistive gas sensors exploiting the change in conductivity.

Experimental

The GaN film (2µm in thickness) used for the sensor fabrication was grown by organometalic vapor phase epitaxy (OMVPE) on c-plane sapphire substrates, with a Si-doping level of ~$1x10^{18}$ cm^{-3}. A pair of rectangular metal pads was evaporated using a Ti (300Å) / Al (1000Å)/ Ti (300Å) / Au (300Å) composite, followed by rapid thermal annealing at 900°C for 60 s in N_2 ambient. Two devices were fabricated with the same ohmic contact geometry of 1mm x 3mm, but different gaps of 0.5mm (exposed active area=1.5 mm^2) and 1.0 mm (exposed active area=3.0 mm^2) between the contacts. After fabrication, the devices were tested in a computer controlled gas sensor test-bed

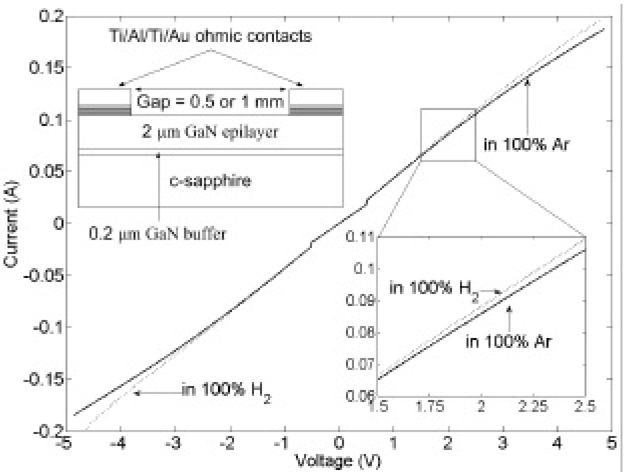

Figure 1. Current versus voltage characteristics of a typical GaN resistive gas sensor. The inset shows the resistive device structure and the blowup around 2Vdc shows the operating region.

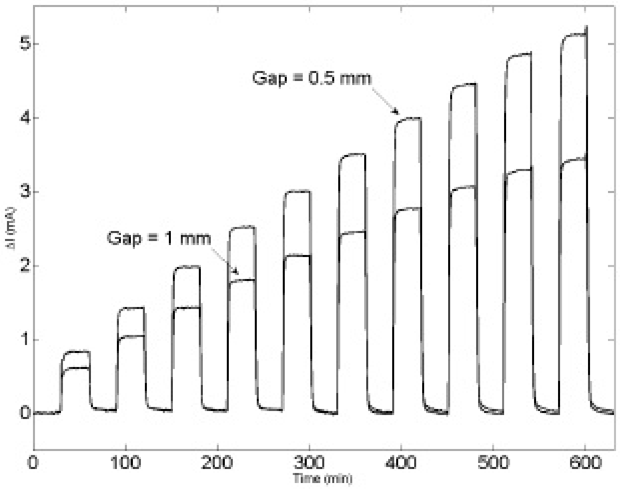

Figure 2. GaN resistive sensor response to 10% to 100% H_2 diluted in Ar in 10% increments at 50°C with Ar purge in-between H_2 concentrations.

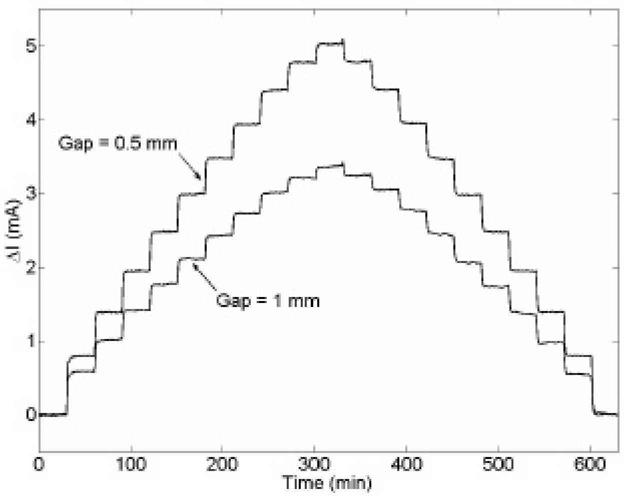

Figure 3. GaN resistive sensor response to 10% to 100% H_2 diluted in Ar in 10% increments at 50°C without Ar purge in-between H_2 concentrations.

described elsewhere [7]. Figure 1 shows the current versus voltage characteristics of a typical GaN resistive gas sensor, verifying the ohmic behavior of the device. Figure 1 also shows a blow up of the I-V curve around the operating voltage of 2 Vdc. A schematic of the device can be seen in the inset in Figure 1. The response is defined as the change of current (ΔI) due to H_2 flow while using a constant 2 Vdc bias.

Results and Discussion

Figure 2 shows the monotonic response to various increasing concentrations of H_2 at 50°C (the lowest isothermal temperature of the test-bed) 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% increments. In contrast to Si hydrogen sensors based on a similar geometry which saturate above ~ 40% of H_2 concentration [7], there is no sign of saturation even for pure H_2 in the GaN resistive sensors. In addition, the sensors show no memory effects after each Ar purge cycle, as evidenced from the clear drop back to zero ? I after each Ar purge. The response time (from the onset of H_2 flow to steady-state) of the GaN sensors is ~7 min, while the time for first response is only ~30 s. For the 0.5 mm gap sensor, the response is ~1.5 times greater than that of the 1.0 mm gap sensor for all H_2 concentrations tested.

In the continuous operation mode where H_2 concentration changes without any Ar purge cycles in-between, the GaN resistive sensors exhibit a very consistent response, as shown in Figure 3. Here the H_2 concentration continuously changes from 10% to 100%, in 10% increments, without an Ar purge in-between at 50 °C. Very clear plateau responses for both the 0.5 mm and the 1.0 mm gap sensors were observed, with reproducibility for both the ramp-up and ramp-down stages of H_2 concentration. There is no indication of saturation, memory effects or distortion of response in this continuous operation mode.

As the H_2 concentration was diluted further, the GaN resistive gas sensors remained operative. Shown in Figure 4 are the responses to low concentrations of H_2 (0.1 to 4.7% in Ar) at 50°C. For both devices, a small response at 0.5% H_2 in Ar can be clearly seen with concentration changes of at least 0.5% being clearly differentiated. In particular, for the 0.5mm 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, Figure 4 shows that the lower detection limit has been reduced to 0.5% H_2 for both devices. Therefore, the GaN resistive sensors remain highly sensitive throughout a range of 0.5% to 100% of H_2 in Ar. Figure 5 shows the average steady state response of both GaN resistive gas sensors as a function of H_2 concentration with the standard deviations shown as error bars. The curves shown in

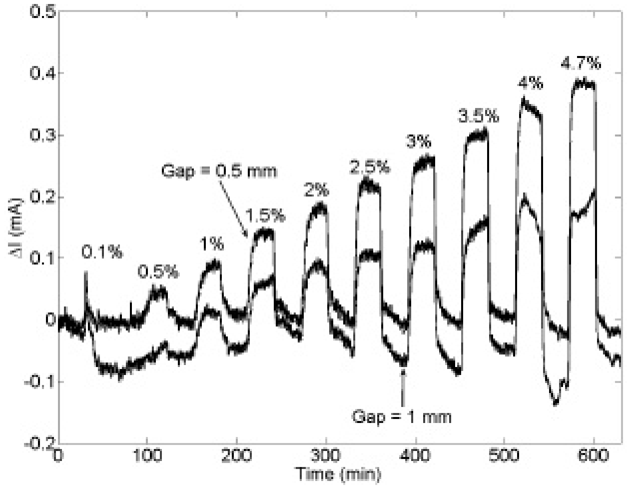

Figure 4. GaN resistive sensor response to 0.1 to 4.7% H_2 diluted in Ar at 50°C with Ar purge in-between H_2 concentrations.

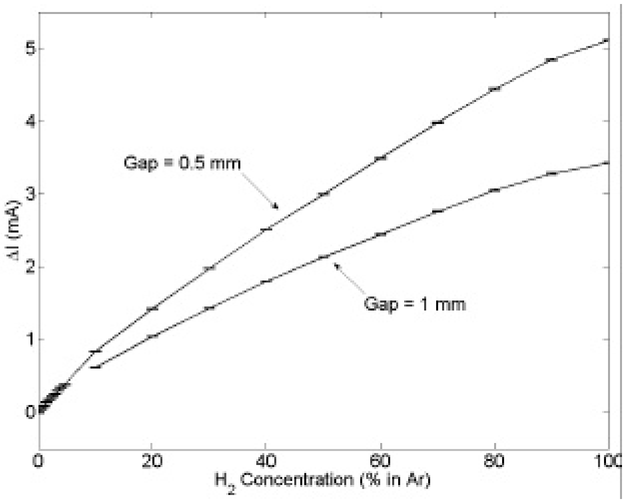

Figure 5. GaN resistive sensor response versus H_2 concentration with Ar as the diluting gas at 50°C.

Figure 5 are not linear over the full range of concentrations but are cubic in nature and can be approximated as linear over relatively small concentration ranges.

The gas sensing mechanism for the GaN resistive sensors discussed here is different from those widely accepted for GaN sensors adopting Schottky and MIS structures, where the creation of a polarized 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 [3,4]. The GaN resistive sensors in this study are free from Pt or Pd gates, and the contacts are covered with a thick layer of Au which is regarded as an inhibitor to H adsorption and diffusion [8]. 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. One 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 [9]. For GaN, this could be achieved either by physisorption at the defective sites and/or surface native oxides, or by passivating the dangling bonds on the GaN surface. In either case, if this were the mechanism responsible for hydrogen sensing, 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, supporting the suggested model. The experimental data observed indicate that surface adsorption is a possible gas sensing mechanism for the observed gas sensor response of the GaN resistive sensors.

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 [10]. Another theoretical work pointed out [11] 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 geometrical dependence, temperature behavior, and doping effects on these GaN hydrogen sensors may elucidate the effects of hydrogen on the electrical properties of GaN and the hydrogen sensing mechanisms.

Summary

In summary, GaN resistive hydrogen gas sensors show wide range sensitivity to H_2, from 0.5% to 100% of H_2 in Ar gas. The response, as measured by the change in current at a constant dc voltage of 2V, is linear with respect to the H_2 content in Ar gas over small concentration ranges, 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. More experimental data are needed to clarify the likely gas sensing mechanisms.

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