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Pt-AlGaN/GaN HEMT-Sensor for Hydrogen Sulfide (H_2S) Detection †

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Abstract: AlGaN/GaN high electron mobility transistor (HEMT)-sensor with a catalytic Pt-gate is fabricated and tested for toxic H_2S gas detection. AlGaN/GaN was chosen to extend the sensor detection range and to be able to operate at temperatures beyond those allowed by state-of-art Si-FET sensors. Testing was performed using a gas mixing apparatus in dry synthetic air ambient. High sensitivity, $\Delta I/I_0$, 8% for 80 ppm and 0.23% for 0.5 ppm H_2S/air, is achieved at a temperature of 250 °C, with a corresponding ΔI of 617 μA and 18 μA, respectively, indicating suitability of the proposed sensor for industrial gas safety detectors.

Keywords: AlGaN; GaN; gas sensor; HEMT; hydrogen sulfide; H_2S; high temperature; 2DEG

1. Introduction

Continuous industrial growth results in rising levels of toxic gas e.g., CO, NO_x, SO_2, NH_3 and H_2S release into the atmosphere, hence emissions control regulations are imposed [1]. Analytical techniques like gas chromatography are suitable for air analysis in a laboratory environment, while for on-site monitoring portable, low-cost gas sensors with high accuracy are necessary [2].

Hydrogen sulfide (H_2S) is a colorless, flammable, toxic gas. It naturally occurs in i.e., volcanic emissions, but also as industrial byproduct of petroleum refinement, food processing or cellulose production [2]. The recommended worker safety threshold limit value (TLV) and permissible exposure limit (PEL) for H_2S are set at 1 ppm and 20 ppm, respectively. Industrial and harsh environments require high-temperature compatible H_2S sensors, therefore semiconductors such as GaN and SiC, due to their wide bandgap, chemical and thermal stability, are promising materials.

Sensing of H_2S by chemiresistive metal-oxide sensors, electrochemical or optical detectors, among others, has been shown [1,2]. By contrast, field effect transistor (FET) based sensors are a promising alternative for low power, miniature sensors compatible with semiconductor manufacturing technology. Previously H_2S sensing with catalytic SiC-FET or GaN Schottky diodes was demonstrated by [3,4], but the reported maximum detection limits were lower than needed for triggering H_2S safety meters. Sensors based on high electron mobility transistors (HEMT) fabricated using AlGaN/GaN heterojunction offer unique advantages of high sensitivity, superior signal amplification, high temperature stability and chemical corrosion resistance.

In this work we report on the design, fabrication and testing of Pt-AlGaN/GaN HEMT-sensor for detection of H_2S gas at elevated temperature, for concentrations ranging from 80 ppm to 0.5 ppm. To our knowledge this is the first report of H_2S sensing with GaN HEMT-sensors.

2. Materials and Methods

Figure 1a shows a schematic cross-sectional view of the studied HEMT-sensor. At the interface of an epitaxially grown AlGaN/GaN heterojunction, a high electron density channel, two-dimensional electron gas (2DEG), is formed, due to the spontaneous and piezoelectric polarization effects [5]. The HEMT operating principle is based on modulating the 2DEG conductance via the gate electrode. When this electrode is fabricated using a catalytic metal, such as Pt or Pd, modulation of 2DEG occurs upon exposure to reducing or oxidizing gases, resulting in a measureable signal shift.

The HEMT-sensors were fabricated on epitaxial structures grown by MOCVD on 2 inch sapphire wafers. The wafers were purchased from Suzhou Nanowin Co. (Suzhou, China) The grown stack, starting from the substrate, consisted of a proprietary nucleation layer, a 1.8 μm GaN buffer, 1 nm AlN interlayer, unintentionally doped 21 nm $Al_{0.26}Ga_{0.74}N$ barrier and 1 nm GaN capping layer. Device fabrication began by performing wet chemical cleaning of the substrates with acetone, isopropanol and DI water rinsing. Afterwards mesa etching was performed by ICP BCl_3/Cl_2 plasma to isolate individual devices. Then ohmic contacts consisting of a Ti/Al/Ti/Au stack with thickness 20/110/40/50 nm, were e-beam evaporated and patterned by lift-off. A 60 s dip in $HCl:H_2O$ solution was done right before loading the wafers into the deposition chamber to etch any surface oxides. After pattering, the contacts were annealed for 47 s at 870 °C in N_2 ambient. The sensing gate electrode was then formed by e-beam evaporation of 10 nm Pt and lift-off followed by evaporation and lift-off of wire bonding metal by-layer of 30/300 nm Ti/Au. The devices were then passivated by depositing 500 nm PECVD SiN_x. Finally, Pt sensing area and bondpad windows were opened by a combination of RIE and BOE etching of the SiN_x.

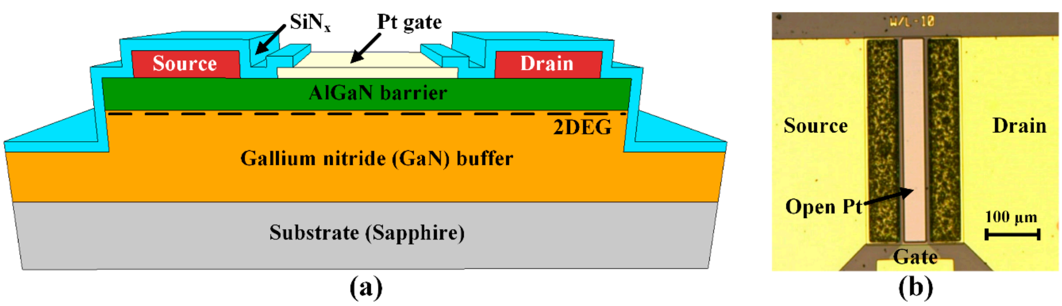

Figure 1. Schematic representation (**a**) and top view (**b**) of fabricated Pt-AlGaN/GaN HEMT H_2S sensor.

An optical microscope image of a completed Pt-HEMT sensor is shown in Figure 1b. The sensing area exposed to the ambient had dimensions of 40 μm × 400 μm and the gate-source and gate-drain spacing was 6 μm.

After fabrication, the wafers were diced into individual devices and wire bonded to ceramic substrates with larger pads. The gas testing was performed using a commercial gas mixing system from Beijing Elite Tech Co., (Beijing, China) which consists of mass flow controllers to dilute the testing gas, a 1.8 L volume chamber with gas inlet/outlet, temperature controlled hotplate, temperature and humidity sensors and electrical feedthroughs. The sensors were tested at 250 °C using H_2S reference gas diluted with dry air (O_2/N_2 = 21%/79%) in the concentration range from 80 ppm to 0.5 ppm. The device output was measured using a pair of Keithley 2450 source meters.

3. Results and Discussion

The correct FET operation of our Pt-AlGaN/GaN sensor with increasing temperature is shown in Figure 2. It is evident that the output characteristics (I_{DS}–V_{DS}) of our Pt-HEMT sensors show clear triode and saturation regions in the examined temperature range (26–250 °C).

Transient response characteristics to injecting H_2S gas in the concentration range from 80 ppm to 0.5 ppm are shown in Figure 3a. The gas injection time and air purge time were kept constant at 25 min during these measurements. Upon exposure to H_2S the source-drain current increases from the baseline value in dry air. The detection mechanism involves the dissociation of H_2S molecules into S and H atoms at the surface of Pt electrode. H atoms subsequently diffuse to the metal-semiconductor interface, where dipoles form and lower the built-in electric field, causing a reduction of the Schottky barrier height and an increase in I_{DS} [6]. The signal repeatability for 20 ppm H_2S is shown in Figure 3b, with gas injection/purge duration of 15/60 min. The inset indicates signal values measured 5 min and 10 min after start of gas injection cycle. The response (t_R) and recovery (t_F) times, required for the sensor signal to rise/fall from 10 to 90% of the steady state for 20 ppm H_2S concentration were t_R = 56 s and t_F = 38.6 min, respectively. The sensor sensitivity (S) is defined as:

$$S = \frac{I_{H_2S} - I_0}{I_0} \times 100\%, \tag{1}$$

where I_{H2S} and I_0 are drain current values in H_2S containing ambient and baseline value in dry air, respectively. Sensitivity for the tested H_2S range is plotted in Figure 4. It is observed that S increased with increasing concentration of the test gas and that the sensor signal did not saturate at low ppm concentrations, contrary to previously reported SiC-FET sensor [3]. An important sensor parameter is the magnitude of sensing signal variation, $\Delta I = I_{H2S}–I_0$. Previously reported gas sensors based on Pt-AlGaN/GaN Schottky diodes showed very high sensitivities, in the order of 10^3% at ppm level gas concentrations, however signal variation was in the nA range, due to low baseline signal values [7]. Low ΔI will result in higher noise susceptibility of the sensor and higher limit of detection. The signal variation of our Pt-HEMT sensors is shown in the inset of Figure 4. At 80 ppm H_2S concentration a substantial response of ΔI = 617 μA was measured, while at 0.5 ppm ΔI = 18 μA, which was larger than the reported value of ΔI ~ 1.1 μA at 1 ppm H_2S at −1 V bias, for a Schottky type sensor [4].

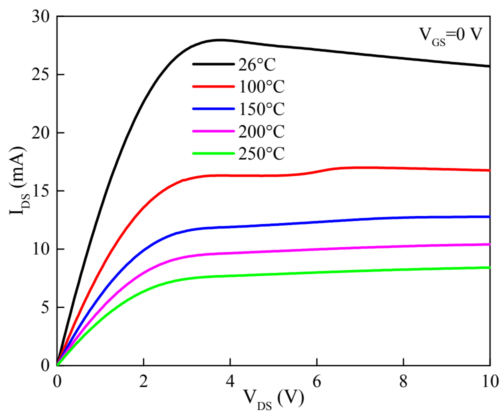

Figure 2. DC output characteristics ($I_{DS}–V_{DS}$) of our Pt-AlGaN/GaN HEMT sensor at different operating temperatures.

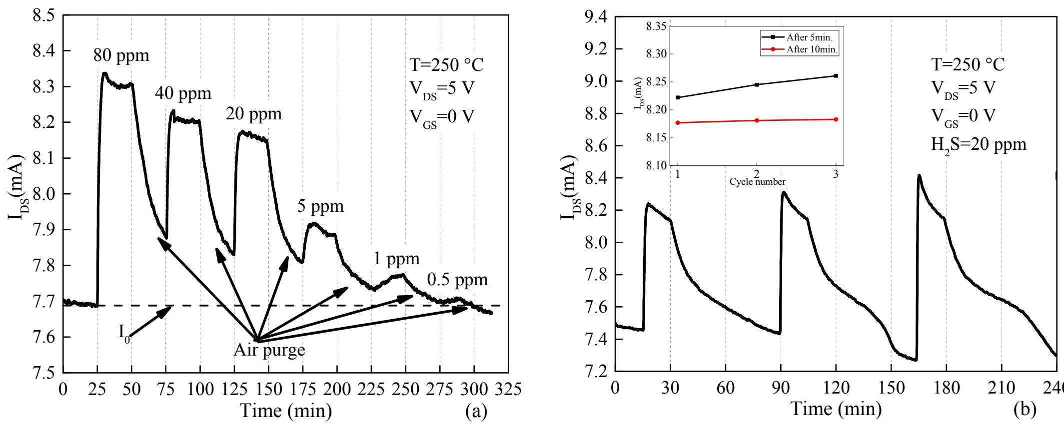

Figure 3. Transient response characteristics of Pt-HEMT sensor at 250 °C with decreasing H_2S concentration from 80 ppm to 0.5 ppm (**a**) and signal repeatability for 20 ppm H_2S concentration (**b**).

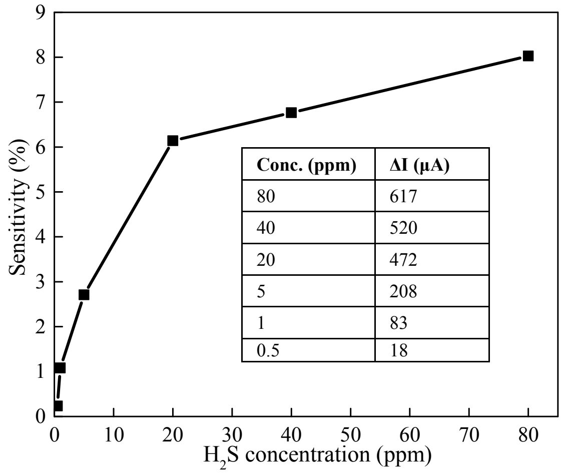

Figure 4. Sensor sensitivity (*S*) at 250 °C versus H_2S concentration. The inset shows measured Δ*I*.

4. Conclusions

In this work, we have demonstrated the detection of H_2S using Pt-AlGaN/GaN HEMT-sensor. An unsaturated response in the tested H_2S/air concentration range at 250 °C, with high sensitivity of 8% at 80 ppm and 0.23% at 0.5 ppm, respectively, as well as large signal variation of 617/18 μA at 80/0.5 ppm were obtained. The high sensitivity and the fast signal response of 56 s for 20 ppm H_2S, indicate the potential for applications of these sensors the in next generation gas safety detectors for harsh industrial environments.

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Conflicts of Interest: The authors declare no conflict of interest.

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