Pt-AlGaN/GaN Hydrogen Sensor With Water-Blocking PMMA Layer

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Abstract—One of the biggest issues with GaN-based hydrogen sensors is their sensitivity to humidity in the ambient. We demonstrate that encapsulation of Pt-AlGaN/GaN Schottky diode with poly(methyl methacrylate) (PMMA) provides effective mitigation of the effects of water. Without PMMA encapsulation, the absolute current signal for detection of 500 ppm of H₂ was decreased by a factor of 8 in the presence of water. By sharp contrast, encapsulated diodes show no decrease in response in the presence of water. The relative current changes are of the order 2.8 × 10⁻⁶ when 500 ppm H₂ is introduced to the surface of bare or PMMA encapsulated diodes in the absence of water or to encapsulated diode in the presence of water. Detection limits of ∼100 ppm H₂ (0.01% by volume) were obtained with standard forward bias detection mode at 1.3 V.

Index Terms—Moisture barrier, hydrogen, sensor, GaN.

I. INTRODUCTION

There is a strong need for robust sensors to monitor leaks in applications where hydrogen is produced or utilized, such as hydrogen-fueled vehicles, aircraft, fuel cells, and industrial processes [1]. Among semiconductor hydrogen sensors, there has been significant work on the use of Pt or Pd-gate metals on GaN-based diodes, which have been shown to be capable of selectively detecting low concentrations of hydrogen at room temperature [2]–[32]. In particular, low concentration detection is valuable since hydrogen is combustible when its concentration in the air reaches or exceeds 4.65% [1], [22]. The hydrogen response mechanism of GaN Schottky diodes involves hydrogen molecule dissociation to atomic form during diffusion through the catalytic Pd or Pt metal to form an adsorbed dipole layer at the metal–semiconductor interface [2], [3], [7], [10], [33]. This hydrogen-induced dipole layer causes a reduction of the effective Schottky barrier height, leading to an increase in the sensing current at fixed applied bias voltage [11]–[17].

GaN sensors can operate at elevated temperatures (as high as 600 °C has been reported [33]) because of their wide bandgap and excellent mechanical and chemical robustness. The use of AlGaN/GaN heterostructures in transistor or diode mode can amplify the hydrogen signal response relative to homostructure diodes, due to the strong effect of surface charges on the two-dimensional electron gas at the AlGaN/GaN interface [5]–[7], [18]–[21]. GaN-based Schottky diodes, metal oxide semiconductor (MOS) diodes, AlGaN/GaN high electron mobility transistors (HEMTs), resistor and GaN nanowires have been developed for hydrogen sensors [2]–[34]. Recently, improvements in sensitivity of AlGaN/GaN diodes have been achieved using Pt nanowire networks with high surface-to-volume ratio as the catalytic Schottky metal [12], [23], [27], as well as using different orientations and surface polarities of the GaN [17], [25]–[26], [35]. For example, the current-voltage characteristics of semipolar GaN diodes remained rectifying after hydrogen exposure, in sharp contrast to the case of c-plane N-polar GaN, where there is a transition to Ohmic behavior [17]. This is due to the fact that hydrogen has a much higher affinity for the N-face surface of GaN than the Ga-face. These results show that the surface atom configuration and polarity play a strong role in hydrogen sensing with GaN [17], [20], [25], [26], [28], [35]. Interfacial oxide layers can also alter the response of GaN Schottky diodes to hydrogen, with diodes prepared in-situ to avoid oxide interfacial layers showing lower responses to hydrogen [10]. The incorporation of an SiO₂ layer to form a metal-oxide-semiconductor structure was found to greatly enhance the sensing response [10], [20], [28].

One of the weaknesses of current GaN hydrogen sensors is the influence of humidity or water on detection sensitivity [31]. Absorbed water molecules have been found to block available surface adsorption sites for hydrogen and thereby reduce the hydrogen detection sensitivity compared to low humidity conditions. The hydrogen detection sensitivity decreases in direct proportion to the relative humidity in the ambient [31]. In this letter, we show that encapsulation with a common polymer film, poly(methyl methacrylate) (PMMA) used in
the semiconductor industry as a component of electron beam resists eliminates this problem. PMMA has a low permeability coefficient for moisture. Given the ease with which it can be spun-on to a surface and patterned, this makes it an attractive candidate as a moisture barrier on GaN-based hydrogen sensors. Recently, it was used in selective hydrogen sensors based on Pd nanoparticle/graphene hybrid and nanocrystalline In$_2$O$_3$-doped SnO$_2$ thin film sensors [36], [37].

II. EXPERIMENTAL

The AlGaN/GaN layer structures were grown on c-plane Al$_2$O$_3$ substrates with a low temperature GaN buffer by metal-organic chemical vapor deposition (MOCVD) as described previously [8], [12], [22]. Figure 1(a) shows a schematic of the layer and device structure. This standard Ga-polar AlGaN/GaN heterostructure had a sheet carrier density of $9 \times 10^{12}$ cm$^{-2}$.

Ohmic contacts were formed by lift-off of e-beam deposited Ti (200 Å)/Al (800 Å)/Ni (400 Å)/Au (800 Å) subsequently annealed at 900 °C for 60 s under a flowing N$_2$ ambient. The surface was encapsulated with 2000 Å of plasma enhanced chemical vapor deposited SiN$_x$ at 300 °C. Windows in the SiN$_x$ were opened by buffered oxide etchant wet etching, and 100 Å of Pt was deposited by e-beam evaporation for Schottky contacts. The final metal was e-beam deposited Ti/Au (200 Å/2000 Å) interconnection contacts.

For spin-coating of PMMA on the device surface, PMMA (molecular weight; 996000) was dissolved in anisole with a concentration of 40 mg/mL, and the solution was mixed for 12 hr. 150 nm of PMMA was coated on the fabricated device as a moisture barrier by spin-coating at 4000 rpm for 30 s [37], and removed on the contact areas for probing. The cross-sectional SEM (scanning electron microscope) image of the 150 nm thick PMMA layer on a silicon substrate is shown in figure 1(b). The reference bare device has the same structure as the encapsulated sensor except for the PMMA layer. Current-voltage (I–V) characteristics of both the uncoated and encapsulated Schottky diodes were measured at 25 °C using an Agilent 4156C parameter analyzer with the sensors in a gas test chamber in ambients of N$_2$, 500 ppm dry hydrogen in nitrogen or the same concentration of hydrogen bubbled through water to produce 100 % relative humidity.

III. RESULTS AND DISCUSSION

Figure 2(a) shows I–V characteristics from unencapsulated diodes before and after exposure to 500 ppm dry H$_2$ in N$_2$. (b) The insets show the same data on a semi-log scale.

The I–V characteristics were unaffected by the presence of the PMMA, and the same absolute and temporal characteristics including response and recovery times were obtained when detecting dry hydrogen. Hydrogen molecules absorbed on the Pt surface dissociate into atoms, which diffuse to the AlGaN interface where the dipoles formation reduces the Schottky barrier height. Thus, at fixed applied bias, the current flowing in the diode increases [2], [3], [7], [10], [33]. The presence of the thin PMMA layer did not affect this process, as shown in figure 2(a) and (b). Over the low forward bias range of the I–V characteristics, the Schottky barrier heights for the diodes were extracted using the thermionic emission model [8], [22], [26]. The reduction in barrier height upon 500 ppm hydrogen exposure was 0.039 and 0.041 eV for the unencapsulated and encapsulated respectively.

Figure 3 shows the relative percentage current change of both bare and encapsulated diodes as a function of bias voltage for exposure to 500 ppm dry H$_2$ or with the same concentration of hydrogen with 100% humidity. Note that the bare sensors suffer a major decrease in sensitivity in the presence of the water vapor content in the hydrogen relative to dry conditions. Water molecules are adsorbed on the catalytic sites of platinum, and prevent hydrogen molecules from being absorbed and dissociated [31]. Meanwhile, the
PMMA encapsulation is completely successful in eliminating this decrease due to the increased humidity level, while still retaining the same absolute detection sensitivity ($\sim 2.8 \times 10^5\%$ at 1.3 V). The PMMA layer is successful in selectively blocking the water molecules while continuing to permit the penetration of hydrogen molecules.

Figure 4 shows the response of bare and encapsulated diodes to three cycles of dry 500 ppm $\text{H}_2$, followed by switching to wet $\text{H}_2$ for 3 cycles and then back to the dry $\text{H}_2$. Note the decrease in response of the bare diode when the wet $\text{H}_2$ is introduced. By sharp contrast, the PMMA encapsulated diodes show the same response to both dry and wet $\text{H}_2$. Finally, 3 cyclic exposures of wet $\text{N}_2$ were introduced to both devices, with no detectable response. The water blocking role of the PMMA layer without decreasing the response to hydrogen is clearly confirmed in figure 4. While PMMA has low permeability coefficients for moisture ($5.0 \times 10^{-11} \text{ cm}^3 \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$), some other common polymers have even lower values, (eg. Poly(vinyl chloride), poly(ethylene) and poly(trifluoro chloroethylene) [38] and therefore are also candidates as encapsulants, although ease of application and compatibility with semiconductor surfaces must be considered. In addition, polystyrene with low mobility with noble metal can be used to ensure the long term stability of the uniform thickness polymer film, and polyimide with higher glass transition temperature be employed to enhance the thermal stability of the moisture barrier film [39], [40].

The sensors showed selectivities of $>270$ for hydrogen over different gases (CH$_4$(4% in N$_2$), CO (0.1% in N$_2$), NO$_2$(0.05% in N$_2$), CO$_2$ (10% in N$_2$) and O$_2$ (100%)) sequentially introduced to the surface. The peak current was logarithmically dependent on hydrogen concentration over the range 0.1-4%, the response time was <4 secs, and the dynamic range for detection was from 0.01-4 at. % of hydrogen in N$_2$. The linearity of response was excellent ($<2\%$ difference in peak current) for detection of 500 ppm wet or dry $\text{H}_2$.

**REFERENCES**


