Structural and electrical sensitivity at several temperatures with hydrogen sensor of Ni/AlGaN Schottky diode

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Abstract. The characteristics of Ni Schottky diodes on AlGaN contact the Al mole fraction up to $x = 0.11$ in pure nitrogen and 2% hydrogen in nitrogen ambient are studied. High temperature stability of Ni diode on AlGaN was achieved by long term annealing at 450°C at 1min. The diode I-V response from (50-450°C) has been characterized, revealing the diodes ability to detect 2% hydrogen in nitrogen ambient at 100°C up to 450°C and pure nitrogen from 150°C up to 450°C. For the samples without annealing under gas of 2% hydrogen in nitrogen ambient, the ideality factor decreases from 1.77 to 1.50, and series resistance decreases from 213 Ω to 126Ω, and the barrier height increases from 1.00 to 1.18 eV with increasing temperature. For the Schottky contacts annealed in nitrogen ambient at 450°C for 1min, the ideality factor decreases from 2.18 to 1.58, and series resistance decreases from 363Ω to 207Ω, and the barrier height increases from 0.77 to 1.04 eV with increasing temperature in a temperature range of 198-298 K. The ideality factor and series resistance of the Schottky contacts with annealing are higher than those without annealing, while the barrier height is lower than that without annealing at various temperatures.

Keywords: Ni Schottky diodes, AlGaN HEMT, Thermal annealing, gas sensors.

1 INTRODUCTION

There is emerging interest in the use of GaN Schottky diodes as sensitive combustion gas sensors (Ambacher, et al., 2002, Casady, et al., 1998, Ekedahl, et al.,1998) and of AlGaN high electron mobility transistors (HEMTs) for chemical sensing (Kim, et al., 2003, Tarakji, et al., 2002, Mehandru, et al., 2005). The high carrier density formed at the AlGaN interface by spontaneous and piezoelectric polarization makes this structure particularly sensitive to changes in surface strain or potential. In addition, the ability to integrate these sensors with HEMT electronics for wireless communication systems is attractive for many applications. Neuberger et al. have suggested that the sensing mechanism for chemical adsorbates originated from compensation of the polarization induced bound surface charge by interaction with the polar molecules in the liquids (Casady, et al., 1998). There is a strong interest in wide band gap semiconductor gas sensors for applications including fuel leak detection in spacecraft. In addition these detectors would have dualuse in automobiles and aircraft, fire detectors, exhaust diagnosis and emissions from industrial processes (Svenningstorp, et al., 1999, Cheng, et al., 2008, Simin, et al., 2002). GaN electronics and sensors will reduce spacecraft launch weighs and increase satellite functional capabilities. Given the high cost per pound of launching payloads into earth orbit, the weight savings gained by using wide band gap devices could have large economic and competitive implications in the satellite industry. Existing commercial satellites require thermal radiators to dissipate heat generated by the spacecraft electronics. These radiators could be eliminated with GaN, and allow greater functionality (more transponders in a commercial satellite) by utilizing the space and weight formerly occupied by the thermal management system. In addition, the radiation hardness of these materials would reduce the weight of shielding normally used to protect spacecraft electronic components from radiation. GaN is capable of operating at much higher temperatures than more conventional semiconductors such as Si. Simple Schottky diode or field-effect transistor structures fabricated in GaN (and SiC) (Chen, et al., 1996) are sensitive to a number of gases, including hydrogen and hydrocarbons (Ayyildiz, et al., 2005). One additional attractive attribute of GaN and SiC is the fact that gas sensors based on this material could be integrated with high-temperature electronic devices on the same chip. There have already been reports of rad-hard (>300 M rad Co-60 gamma ray tolerance) Combustion gas detectors with extremely fast time response and capable of operating at high temperatures, eliminating bulky and expensive cooling systems.

The device structures were mainly based on simple Schottky diodes with Pt contacts (Neuberger, et al., 2001, Eickhoff, et al., 2003, Luther, et al.,1999). Metal-oxide-semiconductor (MOS) diode on an AlGaN have much higher sensitivity than Schottky diodes on the GaN layer, because they are true transistors and therefore operate with gain, significantly better thermal stability than a metal–gate structure (Hunter, et al.,1995, Hunter, et al., 2002, Kim, et al., 2003) and is well-suited to gas sensing. When exposed to changes in ambient, changes in the surface potential will lead to large changes in channel current. High temperature operation and long term stability are important requirements for gas sensors. Hydrocarbons are dissociated by catalytic metals only at elevated temperatures, making it necessary for hydrocarbon gas sensors to be operated at these temperatures. Gas sensors based on Si cannot be operated above about 250°C, prohibiting them from being used as hydrocarbon detectors or for other applications requiring high temperature operation. On the other hand, semiconductors with wider bandgaps retain their semiconducting properties at higher temperatures and can therefore be operated as gas sensors at higher temperatures. The sensors must also be able to withstand operation in the high temperature environments present in many applications. Pt-SiO-SiC gas sensors have been operated at temperatures as high as 800°C by adding a TaSi layer to the device structure improving the stability of the Pt layer (Baranzanhi, et al., 1995). Pd Schottky contacts on SiC have been observed to react at temperatures as low as 425°C, forming Pd silicides (Ambacher and et al, 2003). Pt Schottky diodes to n-type GaN have been observed to react at temperatures as low as 300°C, this observation is in agreement with observations of O_2 assisting in the removal of hydrogen from similar sensors, most likely by the formation of H_2O, which then leaves the sample more rapidly than hydrogen atoms (Ambacher and et al, 2003). AlGaN is a wide-bandgap semiconductor Eg = 6.2 eV that shows great promise for electronic devices operating at high temperatures. In this report, Ni Schottky diodes to AlGaN are described. The response of the diodes to air, nitrogen and hydrogen at temperatures from 30-500°C and the thermal stability of the diodes during long term annealing at 800°C have been investigated. The results indicate that Ni diodes on AlGaN appear promising for hydrogen detection in this temperature range.

2 EXPERIMENTAL details

The AlGaN was first treated surfaces were prepared by the following procedure. Prior to the metal deposition, the native oxide was removed in the NH_4OH: H_2O = 1:20 solution, follow by HF: H_2O = 1:50. Boiling aqua regia (HCl: HNO_3 = 3:1) was used to chemically etch and clean the samples. Followed by the deposition of 100 nm of Ni by sputtering through a shadow mask to form contacts .The structure of the AlGaN gas sensor is shown in Fig. 1. For Ohmic contact, Al electrodes were deposited on the front surface of the substrate and Ni for the heater was deposited on the backside. All samples were annealing from 600-800°C for 15min. Gas sensing experiments were carried out in a homemade Chamber with operating temperatures using air, nitrogen and hydrogen at temperatures from 30-500°C at a total pressure of 1 atm. AlGaN sample was mounted on a test fixture with tungsten probes making contact to a Ni diode.

The test fixture was inserted into the chamber with wires leading from the probes through electrical feedthroughs to a Keithley source-measurement unit for current–voltage *I–V* measurements. To investigate the sensitivity of the Ni-coated AlGaN to hydrogen molecules, an apparatus was set up as shown in Fig. 2. The devices were bonded to electrical feed through and exposed to different gas ambients in an environmental chamber (Hunter, et al.,1995, Hunter, et al., 2002, Neuberger, et al., 2001).

3 RESULTS AND DISCUSSION

Fig. 3 presents the reverse current-voltage (I-V) curves at room temperature of the Ni/AlGaN Schottky contacts without annealing and annealed for 1 min in pure N_2 and in a 2% H_2/98% N_2 atmosphere. It is clear that the reverse leakage current is increased after annealing upon introduction of the H_2, through a lowering of the effective barrier height.

The H_2 catalytically decomposes on the Ni metallization and diffuses rapidly though the underlying oxide to the interface where it forms a dipole layer (Tarakji, et al., 2002). At 2.5V forward bias the change in forward current upon introduction of the hydrogen into the ambient is; 4.75mA or equivalently 0.2V at a fixed current of 3mA. This is roughly double the detection sensitivity of comparable GaN Schottky gas sensors tested under the same conditions (Eickhoff, et al. 2003), confirming that the Ni/AlGaN based diode has advantages for applications requiring the ability to detect combustion gases even at room temperature. As the detection temperature is increased, the response of the Ni/AlGaN diodes increases due to more efficient cracking of the hydrogen on the metal contact. The response of Ni diodes on AlGaN upon exposure to a 2% hydrogen gas mixture at 30°C and 180°C has been investigated and the results are shown in Figure 3. It is known that hydrogen can only be detected at elevated operating temperatures for the SiC based devices (Arbab, et al., 1993) and operating temperature of Pt/GaN (Ambacher, et al., 2003). This was confirmed for our Ni diodes on AlGaN, where the diode *I–V* curves changed in a way consistent with a lowering of the barrier height. The high temperature reliability of these samples was tested by holding the diodes at 450°C in N_2 or 2% H_2 in N_2 and measuring their *I–V* characteristics intermittently. Ni/AlGaN samples were tested separately at 450°C, without annealing and annealed in nitrogen ambient for 1min. The dio thermal treatment as before.

The ideality factor n is calculated from the slope of the linear region of the ln *I-V* plot at small forward current and can be written as n=(q/kT)(dV/d(lnI)), where k is the Boltzmann constant, q the electronic charge, and T is the absolute temperature. Figure 4 shows the temperature dependence of the ideality factor without annealing and annealed in 2% hydrogen in nitrogen ambient for 1min. The dashed curves represent the theoretical temperature dependence of the ideality factor. The variation of series resistance R_s as a function of temperature without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min is shown in Fig. 5. For the Schottky contacts without annealing, series resistance decreases from 213Ω to 126Ω with increasing temperature. For the Schottky contacts annealed under 2% hydrogen in nitrogen for 1min, series resistance decreases from 363Ω to 207Ω with increasing temperature. The increase of R_s with the decreasing temperature results from increase of the ideality factor (as trends are similar) and/or lack of free-charge charge carriers at lower temperature (Luther and Wolter,1999).

The barrier height $q\Phi_{B0}$ is obtained from $q\Phi_{B0}=kT\ln(AA^{**}T^2/I_0)$ with TE theory, where I_0 is the saturation current determined by the intercept of the straight line at small forward current on vertical axis in Fig. 3, A is area of diode, and A^{**} is Richardson constant. The theoretical value of A^{**} is 40.44 $Acm^{-2}k^{-2}$ (Donoval, et al., 1991). Temperature dependence of the barrier height is shown in Figure 5. For the Schottky contacts without annealing, the ideality factor decreases from 1.77 to 1.50, and the barrier height increases from 1.00 to 1.18 eV with increasing temperature. For the Schottky contacts annealed for 1 min, the ideality factor decreases from 2.18 to 1.58, and the barrier height increases from 0.77 to 1.04 eV with increasing temperature. Both the decrease in n and the increase in $q\Phi_{B0}$ with increase in temperature are indicative of deviation from the pure TE mechanism. The possible reason could be extra current caused by tunneling through the barrier or the lateral inhomogeneity of the barrier height. The ideality factor of the I-V characteristics dominated by TFE can be expressed as (Kim, J.,2003):

$$n = \frac{E_{00}\coth\left(\frac{E_{00}}{kT}\right)}{(1-\beta)kT} \quad (1)$$

where β is the bias coefficient of the barrier height. We fitted Eq. (1) to the experimental temperature dependence of the ideality factor n. For the Schottky contacts without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min, there were two very good agreements between the experimental datum points and the simulated ones, as shown in Fig. 6. This demonstrated that the dominant mechanism of current flow is TFE. The best fits were obtained for the following parameters: for the Schottky contacts without annealing, E_{00}=19.3meV, β=0.210, for the Schottky contacts annealed for 1 min, E_{00}=36.0 meV, β=0. From I-V curves. The value of E_{00} of the annealed sample is greater than that of the non-annealed one, which shows that there is larger tunnel transmission probability for the Schottky contacts with annealing than that without annealing under 2% hydrogen in nitrogen ambient.

This observation indicates that Ni and AlGaN reacted and AlGaN diffused to the contact surface where it was oxidized by oxygen in the annealing environment. The variations in the annealing behavior of Ni diodes on AlGaN could be due in part to different AlGaN material being used in the studies, the surface morphology and change in these surface properties for different exposed of gas and operating temperatures were studied using SEM as show in Fig. 7. Note for SEM images in Fig. 7 that the surface starting was smoothing in step of as deposited, whereas the land white show on the surface at step of operating temperature under air, the land white become big and clear at steps of gas exposed for N_2 and H_2, these due to change of barrier height and the electrical properties like sensitivity, resistance and response signal will change.

If AlGaN-based Schottky contacts gas sensors could be operated at temperatures near 450°C, similar to SiC MOS gas sensors, rather than at 400°C and to GaN gas sensor near to 600°C improvements in their gas sensing characteristics might be observed. Enhanced sensitivity of hydrogen may also result at higher temperatures. However, it is unlikely that the simple Ni/AlGaN diode will be adequate for stable operation at 450°C.

4 CONCLUSION

In conclusion, Ni/AlGaN diodes appear well-suited to combustion gas sensing applications. The changes in forward current are approximately double those of simple GaN Schottky diode gas sensors tested under similar conditions and suggest that integrated chips involving gas sensors and Ni based circuitry for off-chip communication are feasible in the AlGaN system. The *I–V* characteristics of the diodes indicate a response to hydrogen at all temperatures studied, while propane is detected only at 350°C and above. For the latter method different material were examined with respect to their hydride and nitride properties. Effective procedures in controlling the properties of AlGaN surface for hydrogen atom to diffusion and oxygen molecules to adsorb was achieved and shown using Scanning Electron Microscopy (SEM). These result; correspond to good I-V characteristics obtain on Ni/AlGaN sensor even at high temperature.

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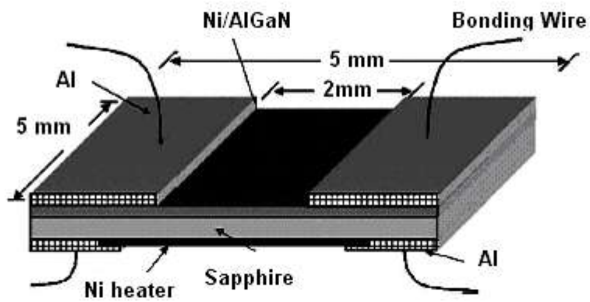


Fig. 1. Structure of a Ni/ AlGaN gas sensor.

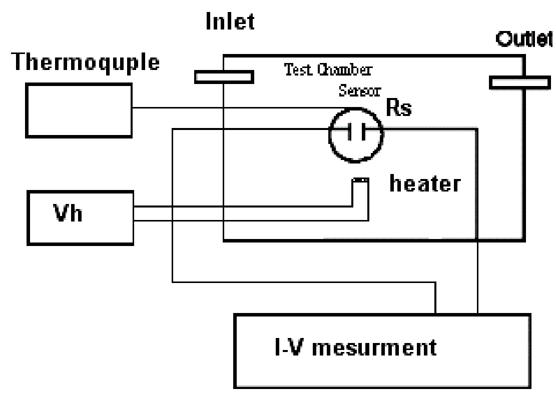


Fig. 2. Schematic diagram for AlGaN gas sensors measurement. V_H: heater voltage; R_S: AlGaN resistance.

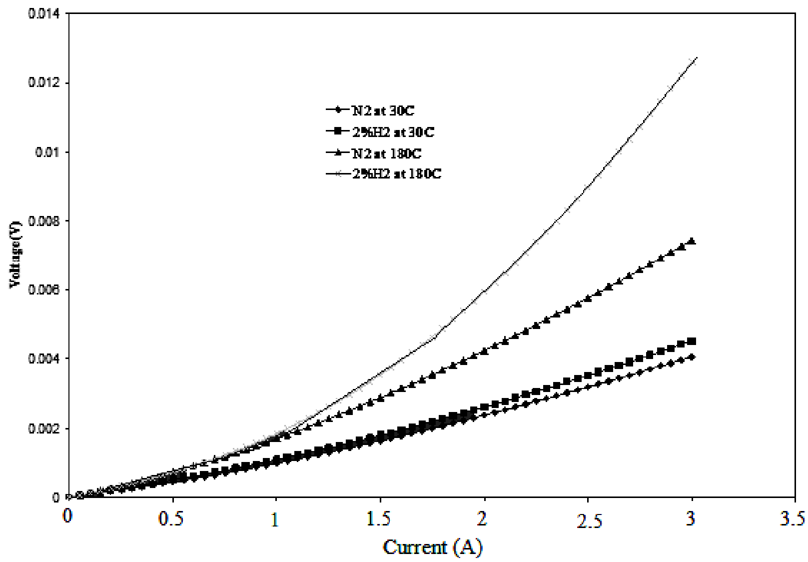


Fig. 3. Reverse *I-V* characteristics at room temperature of the Ni/AlGaN Schottky contacts without annealing and annealed in pure N_2 or 2% H_2 in nitrogen ambient at 450°C for 1min.

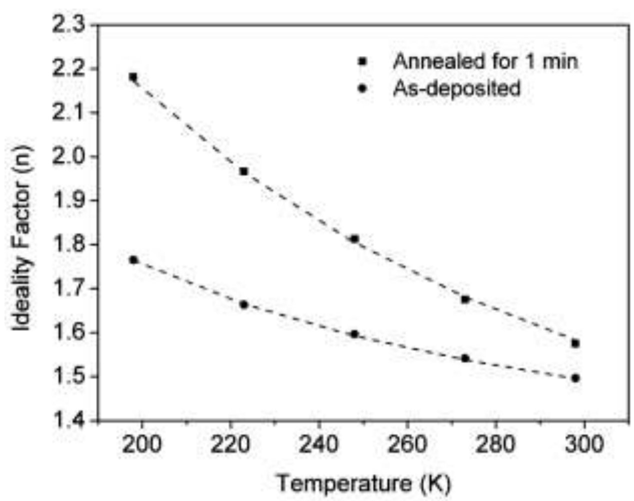


Figure 4: Temperature dependence of the ideality factor of the Schottky contacts without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min. The dashed curves represent the theoretical temperature dependence of the ideality factor.

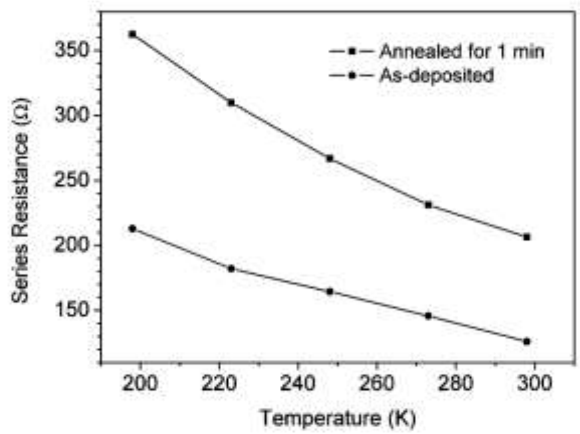


Figure 5: Temperature dependence of series resistance of the Schottky contacts without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min.

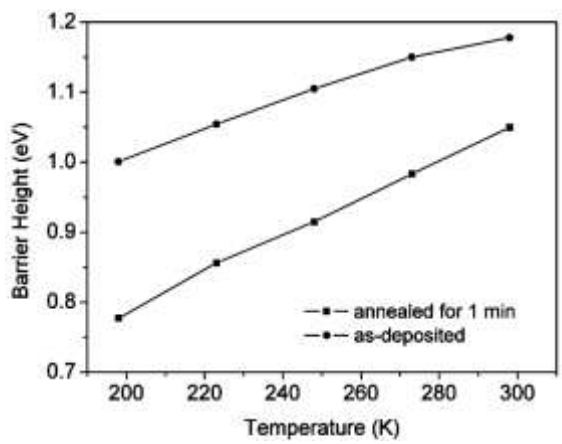
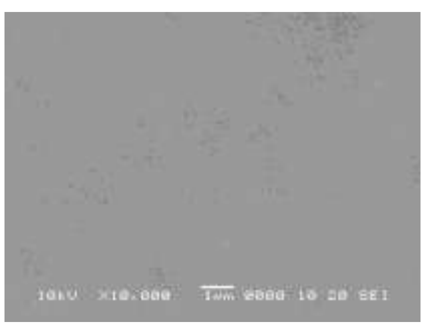
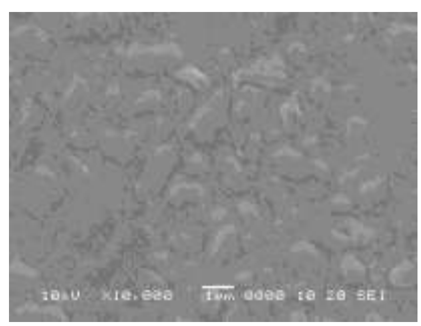


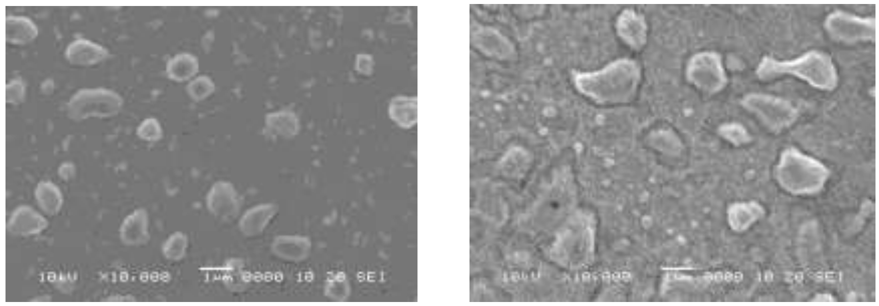
Figure 6 : Temperature dependence of the barrier height of the Schottky contacts without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min.



a) as deposited



b) at 400°C under air



c) at 400C under N2 gas   d) at 400C under $2\%H_2/98\%N_2$

Fig. 7. Variations of surface morphology as shows of SEM images of Ni/AlGaN Schottky contacts without annealing and annealed in 2% hydrogen in nitrogen ambient for 1 min.