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Pt Schottky Diode Gas Sensors Formed on GaN and AlGaN/GaN Heterostructure

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Abstract

Exposure of Pt/GaN and Pt/AlGaN/GaN Schottky diodes to H₂ gas at moderately high temperatures around 100 °C resulted in marked increase of forward and reverse currents. Increase was much larger in the Pt/AlGaN/GaN diode than in the Pt/GaN diode. Rapid turn-on responses and somewhat slower turn-off responses were observed with reproducible response magnitudes. A rigorous computer simulation of I-V curves indicated that current changes are due to changes in the Schottky barrier height caused either by H-induced formation of interfacial dipole or by hydrogen passivation of interface states.

Keywords: GaN, AlGaN, Pt, Schottky, gas sensor

1. Introduction

Hydrogen gas sensors working at high temperatures are demanded for applications such as combustion control and leak detection. GaN-related materials with wide energy gaps maintain semiconducting properties at high temperatures, making them suitable for sensors operating at high-temperatures. However, only few works have been reported on GaN gas sensors [1, 2] with an unclear sensing mechanism.

This paper investigates H₂ gas-sensing characteristics of Pt/GaN and Pt/AlGaN/GaN Schottky diodes. The latter structure is suitable for integration of sensors with HFET circuits on the same chip. Pt was chosen because of its catalytic nature.

2. Experimental

As shown in Fig.1, circular Pt Schottky diodes with Ti/Al/Ti/Au ohmic ring electrodes were fabricated on an n-GaN layer with a carrier concentration of $3 \times 10^{17}$ cm⁻³ and on an Al₀.2₅Ga₀.₇₅N/GaN heterostructure with a sheet carrier concentration of $1.7 \times 10^{13}$ cm⁻² and a Hall mobility of 620 cm²/Vs at RT. Pt Schottky contacts with a thickness of 75 nm and a diameter of 600 µm were formed by electron-beam evaporation after surface treatment in HF solution.

Gas sensing characteristics were measured in a chamber with a base pressure of 0.5 Torr. Each diode was fixed on a ceramic heater and high-purity H₂ gas was introduced into the chamber. Current-voltage (I-V) characteristics were measured by Agilent 4156A semiconductor parameter analyzer.
3. H₂ Sensing Characteristics

Both Pt/GaN and Pt/AlGaN/GaN diodes showed good rectifying behavior at RT with a Schottky barrier height (SBH) of 0.80 - 1.02 eV. Typical I-V characteristics measured before and after exposure to H₂ at 100 °C are shown in Figs. 2(a) and (b) for GaN and AlGaN/GaN diodes, respectively. As seen in Fig. 2, these devices showed remarkable increase of forward and reverse current upon exposure to H₂. Particularly, current increase of the AlGaN/GaN diode was much larger. These diodes maintained good rectifying behavior after high temperature annealing at 630 °C for 1 min in N₂ flow similarly to a recent report [3].

H₂-induced current increase, ΔI, is plotted in Fig. 3 vs. H₂ pressure for an AlGaN/GaN diode held at V=-2V and T=100 °C. ΔI rapidly increased linearly with pressure in the low-pressure region and then showed saturation at pressures higher than 5 Torr. Liu et al [4] and Chen et al [5] reported similar characteristics for Pd/InP and Pd/GaAs Schottky diodes.

Figure 4(a) shows on-off responses of the AlGaN/GaN diode taken at V=-2V and T=80-120 °C. Even at such moderately high temperatures, the device showed steep increase of current in about 10 seconds upon hydrogen exposure. The turn-off responses were slower, being 40-50 seconds. The diode showed similar on-off responses even at RT with reduced response speed and sensitivity. Luther et al [1] and Kim et al [6] reported similar asymmetric on-off responses for Pt/GaN and Pd/GaN diodes. Figure 4(b) shows a cyclic time response of current for the AlGaN/GaN diode taken at V=-2V and T=100 °C. Again, a rapid turn-on response was observed in each cycle. Observed highly reproducible magnitudes of current response for each cycle promise a stable sensing operation.

4. Possible Sensing Mechanism

Hydrogen molecules are known to dissociate on the Pt surface, forming atomic hydrogen. Such atomic hydrogen diffuses through the Pt layer and they are adsorbed at the Schottky interface. Since diodes showed reversible responses to H₂ exposure, creation or passivation of bulk shallow donors by hydrogen in GaN and AlGaN layers is unlikely. I-V characteristics in Fig. 2 suggest that the sensing mechanism is hydrogen-induced SBH reduction.

In order to confirm this, rigorous I-V simulation based on the thin surface barrier (TSB) model for nitride Schottky diodes [8] was performed. Here, ionized surface donors related to nitrogen vacancies reduce the Schottky barrier width and allow transport by thermionic emission, thermionic-field emission and field emission processes. This simulation program has recently reproduced experimental I-V characteristics of GaN and AlGaN Schottky diodes measured by us [9] as well as those measured by other workers [10].

Figure 5 shows experimental and simulated I-V characteristics of a Pt/GaN diode before and after the H₂ exposure at 100 °C. We obtained excellent fitting before H₂ exposure by assuming an exponentially decaying distribution of surface defect donors with a characteristic decay depth δ as shown in the inset of Fig. 5. Then, the experimental I-V curve after H₂ exposure could be reproduced completely by simulation, if one assumes SBH reduction of only 30 meV. Such a change of SBH can be either due to H-induced formation of interfacial dipole, or to hydrogen passivation of interface states causing Fermi level pinning at the Schottky interface. For example, a monolayer thick interfacial dipole layer formed by adsorbed and ionized atomic hydrogen with adsorption sites densities in the range of 10^{12} to 10^{13} cm⁻² can explain the observed SBH change. The observed saturation of ΔI with respect to H₂ pressure and to H₂-exposure time as seen in Figs. 3 and 4, can be explained by a limited number of the adsorption sites in the interface region, although a further study is needed to clarify the exact nature of the adsorption site.

As for the response speeds, the observed asymmetry of the on-off responses indicates that
the rate limiting processes for current rise and fall in our diodes are most likely the hydrogen adsorption and desorption, respectively, at the interface, since H atoms are expected to diffuse through the Pt layer very rapidly similarly to hydrogen diffusion in Pd [7]. Then, the observed on-off symmetry can be explained by assuming that the adsorption process is a chemisorption process accompanying a reduction of the chemical potential for H atoms similarly to the models proposed by other groups for Pd/SiO₂/Si and Pd/n-InP interfaces [11, 12]. Then, desorption requires thermal energy supply, leading to a longer recovery time than adsorption. The observed temperature dependence of current response is obviously consistent with this model.

5. Conclusion

Pt Schottky diodes on GaN and on AlGaN/GaN heterostructure showed increase of forward and reverse currents on exposure to H₂ gas with a much larger increase in the AlGaN/GaN diode. Rapid turn-on responses and slower turn-off responses were observed with reproducible response magnitudes. A rigorous computer simulation of I-V curves indicated that observed current changes are due to changes in Schottky barrier heights, associated either with formation of interfacial dipole or passivation of interface states.

References

Fig 1. Structures of Pt/GaN and Pt/AlGaN/GaN Schottky diodes used in this study.

Fig 2. Typical I-V characteristics of (a) Pt/GaN and (b) Pt/AlGaN/GaN Schottky diodes before and after exposure to H₂ at 100°C.

Fig 3. Current change, ΔI, at V = -2V at 100°C as a function of H₂ pressure for a Pt/AlGaN/GaN Schottky diode.

Fig 4. (a) Time response of current at a reverse bias of -2 V and (b) cyclic time response of current at T=100°C and V=-2V for the Pt/AlGaN/GaN Schottky diode.

Fig 5. Experimental (symbols) and calculated (solid lines) I-V characteristics of a Pt/GaN diode before and after the H₂ exposure at 100°C.