Hydrogen Response of Pd Schottky Diodes Formed on AlGaN/GaN Heterostructure

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(Received 14 October 2005; Accepted 2 November 2005; Published 14 November 2005)

Basic H$_2$ gas-sensing characteristics of Pd Schottky diodes formed on the AlGaN/GaN heterostructure were investigated in vacuum. By introducing a novel surface control process to reduce reverse leakage currents, an unprecedented high H$_2$ sensitivity was achieved where 1 Torr hydrogen caused five orders of magnitude change of current. Surprisingly, the surface control process did not change the C − V characteristics which showed an unexpectedly large shift 1000 mV on H$_2$ exposure. Transient waveforms were almost exponential for the logarithm of current, and response speed increased with increase of H$_2$ pressure and temperature. These results were explained in terms of Schottky barrier height due to adsorption of atomic hydrogen generated by Pd together with a due consideration of the current transport mechanism under reverse bias. [DOI: 10.1380/ejssnt.2005.314]

Keywords: Schottky diode; palladium; hydrogen sensor; AlGaN/GaN

I. INTRODUCTION

In view of increased use of fuel cells in the near future as a new clean and viable energy source replacing petroleum, gas sensors for sensing hydrogen are strongly demanded to avoid hazardous explosion. If one takes account of the recent rapid progress of the so-called sensor networks [1], it is preferred that the sensor material is a semiconductor which can realize an integrated wireless sensor chip where nanometer-sized sensors are integrated on chip with ultra-low-power electronics and low power wireless communication circuits such as used for RFID chips [2].

GaN-related materials have wide energy gaps and maintain their semiconducting properties at high temperatures. They are chemically stable and environmentally friendly. For these reasons, they are potentially suited to sensor application in addition to blue/UV photonic applications and high-power heterostructure field effect transistor (HFET) application. In fact, there are several reports on GaN-based hydrogen sensors [3–5]. Among them, we investigated the Pt Schottky diode-type H$_2$ gas sensor formed on the AlGaN/GaN heterostructure surface in view of possible integration of sensors with HFET circuits on the same chip. However, it did not exhibit high sensitivity at room temperature due to large leakage currents. We also proposed the H$_2$ gas sensing mechanism, but it could not be established due to poor performance.

The purpose of the present paper is to investigate hydrogen gas-sensing characteristics of Pd Schottky diodes formed on AlGaN/GaN heterostructure. Pd was chosen as the barrier metal because of its catalytic nature similarly to Pt. To reduce leakage currents, a novel surface control process has been introduced. From a basic standpoint of elucidation of the sensing mechanism, hydrogen sensing characteristics were investigated in vacuum. A large improvement of sensitivity as well as important information on the sensing mechanism has been achieved.

II. EXPERIMENTAL

As shown in Fig. 1, circular Pd Schottky diodes with Ti/Al/Ti/Au ohmic ring electrodes were fabricated on an Al$_{0.25}$Ga$_{0.75}$N/GaN heterostructure with a sheet carrier concentration of 0.8 × 10$^{13}$ cm$^{-2}$ and a Hall mobility of 950 cm$^2$/Vs at RT. Pd Schottky contacts with a thickness of 75 nm and a diameter of 600 µm were formed by electron-beam deposition after surface treatment in HF solution.

Gas sensing characteristics were measured in a chamber with a base pressure of 0.05 Torr by rotary pump system. The diode was fixed on a ceramic heater and high-purity H$_2$ gas was introduced into the chamber. Current-voltage ($I − V$) and Capacitance-voltage ($C − V$) characteristics were measured by Agilent 4156A semiconductor parameter analyzer and Agilent 4192A impedance analyzer.

III. EXPERIMENTAL RESULTS

A. Leakage current reduction by a new surface control process

Since Schottky diode type sensor devices operate, in general, at reverse bias voltages, it is necessary that their reverse leakage currents before hydrogen exposure are sufficiently small. However, nitride-based Schottky diodes are known to exhibit large leakage currents, and this was the reason why our previous Pt/AlGaN/GaN diode [5]...
showed only a small detection sensitivity. As the operation temperature is increased, the leakage current becomes larger, and prevents sensing operation or increases power consumption beyond the permissible limit.

Thus, we tried to reduce leakage currents by applying a novel surface control process before deposition of Pd. In this connection, our thin surface barrier (TSB) model [6–9] on leakage currents in nitride-based Schottky diodes has indicated that unintentional donors near the surface are the cause of large leakage current. Thus, the idea of the new process was to reduce nitrogen-vacancy related deep donor and oxygen shallow donors. Figure 2 shows the sequence of our new surface control process, the sample surface was irradiated with a N* radical beam at 300°C in an attempt to reduce near-surface nitrogen vacancies. Then, a thin (~1 nm) Al film was deposited at room temperature by a molecular beam deposition process in a MBE chamber. Subsequently, the sample was annealed in an ultrahigh vacuum for 10 minutes at 700 °C in an attempt to getter oxygen atoms out from the AlGaN layer. This process turns the Al layer into an AlOx layer. Finally, the AlOx was removed by HF solution.

The Pd Schottky electrode was formed on AlGaN/GaN heterostructure after applying the above surface control process. I – V characteristics at room temperature are compared in Fig. 3 for the diodes with and without the surface control process. It is seen that the reverse leakage currents are reduced by as large as about five orders of magnitude at $V = -1$ V by applying the present surface control process.

B. Hydrogen sensing characteristics

1. Effect of H2 exposure on Schottky I – V characteristics

Changes of the I – V characteristics caused by exposure to H2 are shown in Figs. 4 (a) and (b) for two Schottky diodes without and with the surface control process, respectively. As seen in Fig. 4 (a), the diode without the surface control showed current increase of about two orders of magnitude at $V = -1$ V upon exposure H2 pressure of 1.0 Torr. On the other hand, current increase of five orders magnitude took place in the case of the diode with the surface control process. This large improvement of sensitivity is obviously due to reduction of the reverse leakage currents as we expected. In fact, we believe that this sensitivity seems to be the highest ever reported for GaN-based Schottky diode type hydrogen gas sensors.

FIG. 2: Sequence of a novel surface control process.

FIG. 3: Change of I – V characteristics before and after the surface control process.

FIG. 4: I – V characteristics on exposure to hydrogen for a diode (a) before and (b) after the surface control process.
2. Effects of hydrogen on $C-V$ characteristics

$C-V$ characteristics of the diodes also showed remarkably large changes upon exposure to hydrogen in vacuum. These changes are shown in Fig. 5 (a) and (b) for the diode without and with the surface control process, respectively. In both cases, they showed large shifts of $C-V$ curves by exposing to $H_2$, keeping the shape of the curve approximately the same. For example, the value of the curve shift on exposure $H_2$ with a pressure of 0.3 Torr was as large as about 1000 mV in both cases. It is surprising that shape of the $C-V$ curves and their shifts on exposure to hydrogen are nearly the same for diodes without and with the surface control process in spite of the large differences of $I-V$ characteristics for these diodes.

3. Transient response characteristics

The observed on-off responses of the reverse current at room temperature are shown for various values of $H_2$ pressure in Fig. 6 for a diode with the surface control process. As seen in Fig. 6, change of current seems to be roughly exponential when the current is plotted in a logarithmic scale vs. the time. The value of its time constant became shorter, as the hydrogen pressure becomes larger, as we had expected. Surprisingly, however, the current saturation level did not depend on the hydrogen pressure.

As for the current recovery after removal of hydrogen, its recovery speed was found to be extremely slow in vacuum, being very different from that of current rise. The speed became much faster when the diode was exposed to air after stopping the hydrogen gas, as also shown in Fig. 6.

The temperature dependence of the current transient curve is shown in Fig. 7. As we had expected, the response speed increased with increase of temperature both for turn-on and turn-off transients. The measured capacitance transient responses are shown in Fig. 8 for different temperatures. We see that the time constant for capacitance change becomes shorter with increase of temperature. However, the saturation capacitance level did not depend on the temperature in spite of the fact that the current saturation level increased with the temperature as seen in Fig. 7.

IV. DISCUSSION ON SENSING MECHANISM

As already mentioned, our group has proposed and verified the TSB model to explain large leakage currents in GaN and AlGaN Schottky barriers [6–9]. In this model, ionized surface donors related nitrogen vacancies reduces the Schottky barrier width and cause current transport through thermionic-field emission. In the case of AlGaN,
there is also a possibility of existence of high densities of oxygen impurity atoms as reported by other workers [10]. Oxygen is known to act as a shallow donor in the AlGaN layer [11, 12]. Thus, it seems highly likely that the reason of the success of our new surface control process in reducing the leakage current is that it reduces the concentrations of nitrogen vacancies and oxygen impurities.

As for the $\text{H}_2$ sensing mechanism, we proposed the following in our previous study on the Pt/AlGaN/GaN hydrogen sensor diode [5]: (1) Hydrogen molecules dissociate on the Pd surface and become atomic hydrogen owing to catalytic action of Pd. (2) Hydrogen atoms diffuse through the Pd bulk layer and are then adsorbed at the Pd/semiconductor interface. (3) Adsorbed hydrogen atoms give up electrons and form an interface dipole layer. This reduces the Schottky barrier height (SBH). (4) Reduction of SBH increases the current through the interface.

The observed shifts of $C - V$ curves without changing the $C - V$ curve shape strongly indicates that the reduction of SBH, changing the threshold voltage for existence of 2DEG. The $C - V$ curves in Figs. 5 (a) and (b) indicate that the magnitude of the hydrogen induced $C - V$ curve shift is nearly the same for the diodes without and with the surface control process. Thus, the obvious problem in applying the above mechanism to the present experimental results is why the large change of SBH did not cause a corresponding large change in the case of the diode without the surface control process. In fact, if one applies the standard thermionic emission (TE) model, SBH reduction corresponding to the current increase in Fig. 4 (a) is calculated to be 200 meV is much smaller than the $C - V$ shift of 1000 mV.

Our explanation of this problem is that the actual current transport mechanism is not the TE transport, but the thermionic field emission (TFE) transport used in the TSB model [6–9]. Due to involvement of tunneling, the current transport becomes less sensitive to SBH in the TFE process as compared with the TE process where the current changed depends exponentially on the SBH change.

After applying the surface control process, unintentional donors in the surface region are reduced, and the mechanism of current transport approaches the TE mechanism. Thus, we see a much larger current change. In the TE transport, the logarithm of the current should be proportional to the change of SBH. Thus, the exponential behavior of the logarithm of current vs. time seen in Fig. 6 can be explained by exponential increase of adsorbed hydrogen at the interface. Such behavior is a typical one for adsorption-desorption processes.

However, there are other unexpected observations in Fig. 6. Namely, the saturation values of current reached during hydrogen exposure were almost independent of on hydrogen pressure at room temperature. Furthermore, the current recovery in vacuum was extremely slow after turn-off of hydrogen. We have recently seen very similar behavior in the Pt/InP hydrogen sensor [13]. These observations can be explained by the fact that the back reaction from atomic hydrogen to molecular hydrogen is extremely slow at room temperature. On the other hand, in the presence of oxygen in the ambient, atomic hydrogen reacts with oxygen, and the recovery response time becomes much faster as seen in Fig. 6.

Thus, all the distinct features of the experimental observation can be explained at least qualitatively by the proposed model, if we take account of the current transport. Future work is, however, necessary to reach the fully quantitative description of the behavior of the present sensor.

V. CONCLUSION

The basic response characteristics in vacuum of a Pd Schottky diode formed on the AlGaN/GaN system have been investigated in view of on-chip integration with HFET circuits. By introducing a new surface control process, the reverse leakage currents of the diode have been reduce a great deal and this has lead to a very high $\text{H}_2$ sensitivity. On the other hand, $C - V$ curves showed nearly the same large shifts of 1000 mV on exposure hydrogen
gas for diodes with and without surface control. Transient response waveforms were almost exponential vs. time for the logarithm of the current, and the response time constant increased with the increase of hydrogen pressure and temperature. All these features can be explained by the hydrogen-induce reduction of SBH with a due consideration of the current transport mechanism under reverse bias.

Acknowledgments

This work is supported in part by the 21st Century COE program at Hokkaido University on "Meme-Media Technology Approach to the R&D of Next-Generation ITs", from MEXT, Japan.

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