English

Research Express@NCKU Volume 4 Issue 2 - April 25, 2008
[http://research.ncku.edu.tw/re/articles/e/20080425/1.html]

Comparative Study of Hydrogen Sensing Characteristics of a Pd/GaN Schottky Diode in Air and N_2 Atmospheres

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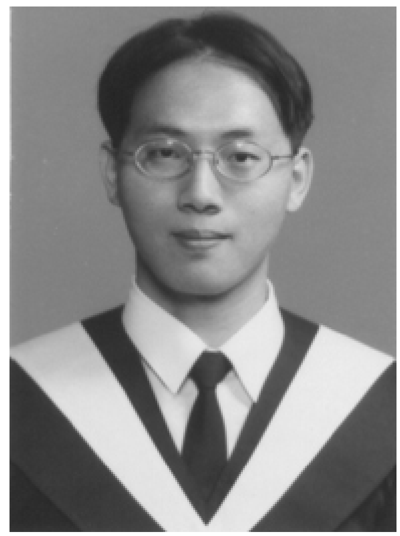
Sensors and Actuators B-Chemical, 123, 1040 (MAY 2007)

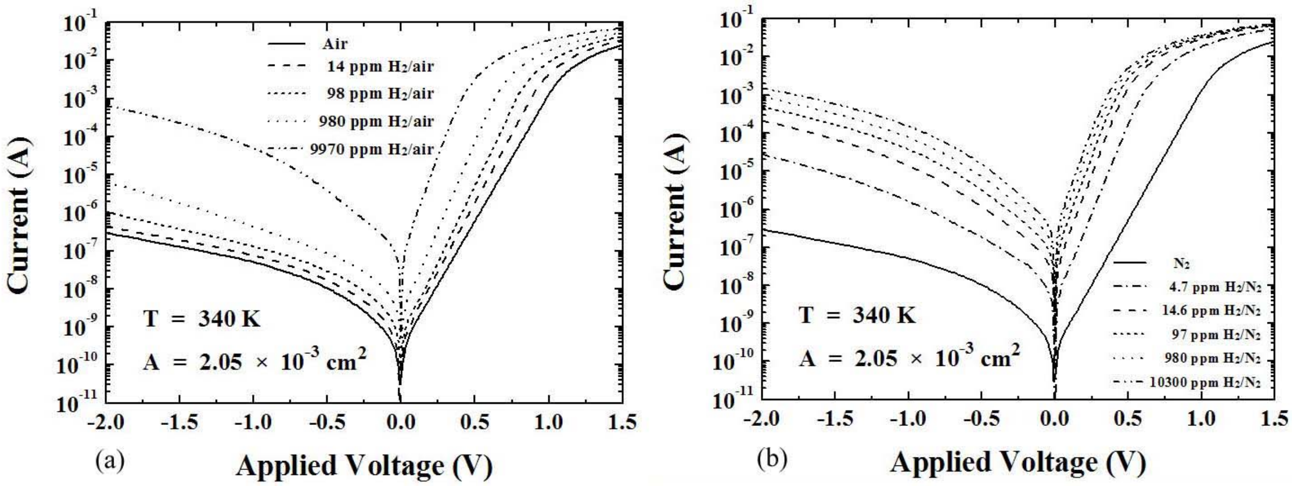


1. Introduction

Due to the progressive and severe requirements in industrial safety and environmental protection, hydrogen sensors have become increasingly important in many applications, e. g., industrial fabrication processes, medical installations, laboratories, and fueled motor vehicles. Wide temperature operation regimes and long term stability are important requirements for gas sensors. Yet, gas sensors based on Si cannot be operated above 200°C, which is directly related to its relatively small band gap (1.12 eV). On the other hand, there is strong interest in developing wide band-gap semiconductor, e.g., GaN (3.4 eV) and 4H-SiC (3.26 eV), hydrogen gas sensors which retain their semiconducting properties and can therefore be operated as gas sensors at higher temperature. However, SiC material is relatively expensive. In this work, the hydrogen sensing and response characteristics of a Pd/GaN Schottky diode at different temperatures have been studied and compared both in air and N_2 atmospheres under steady state and transient conditions.

2. Experiments

The studied device structure consisted of a 2 μm thick undoped GaN buffer layer and a 0.5 μm Si-doped GaN active layer with a carrier concentration of 2×10^{18} cm^{-3}. After epitaxial growth, the devices were etched by an inductively-coupled-plasma reactive ion etch (ICP-RIE) system for mesa isolation. The native oxide on the wafer was removed by the solution of HCl : H_2O = 1 : 1. The Ohmic contact was formed by evaporating 1000 Å Ti/Al metals and annealed by a rapid thermal annealing at 900°C for 90 s in N2 ambience. Finally, Schottky contacts were produced by the evaporation of 350 Å Pd metal. The Schottky contact area was 2.05×10^{-3} cm^2.



Figures 1(a) and 1(b):
The current-voltage (I-V) characteristics of the studied Pd/GaN Schottky diode measured under the atmospheric condition when exposing to different-concentration hydrogen gases balanced with (a) air and (b) N_2 at 340 K.

3. Results and Discussion

Figures 1(a) and 1(b) show the current-voltage (I-V) characteristics of the studied Pd/GaN Schottky diode measured under the atmospheric condition, and exposed to different-concentration hydrogen gases balanced with air and N_2 at 340 K. Both forward and reverse currents in air and N_2 atmospheres are increased with increasing the hydrogen concentration. Obviously, the device can be operated under bipolarly applied biases and exhibits a remarkable hydrogen detection capability over varied hydrogen concentrations both in air and N_2 atmospheres. Furthermore, even at an extremely low hydrogen concentration of 14 ppm H_2 in air or 4.7 ppm H_2 in N_2 at 340 K, the available current variation can be detected.

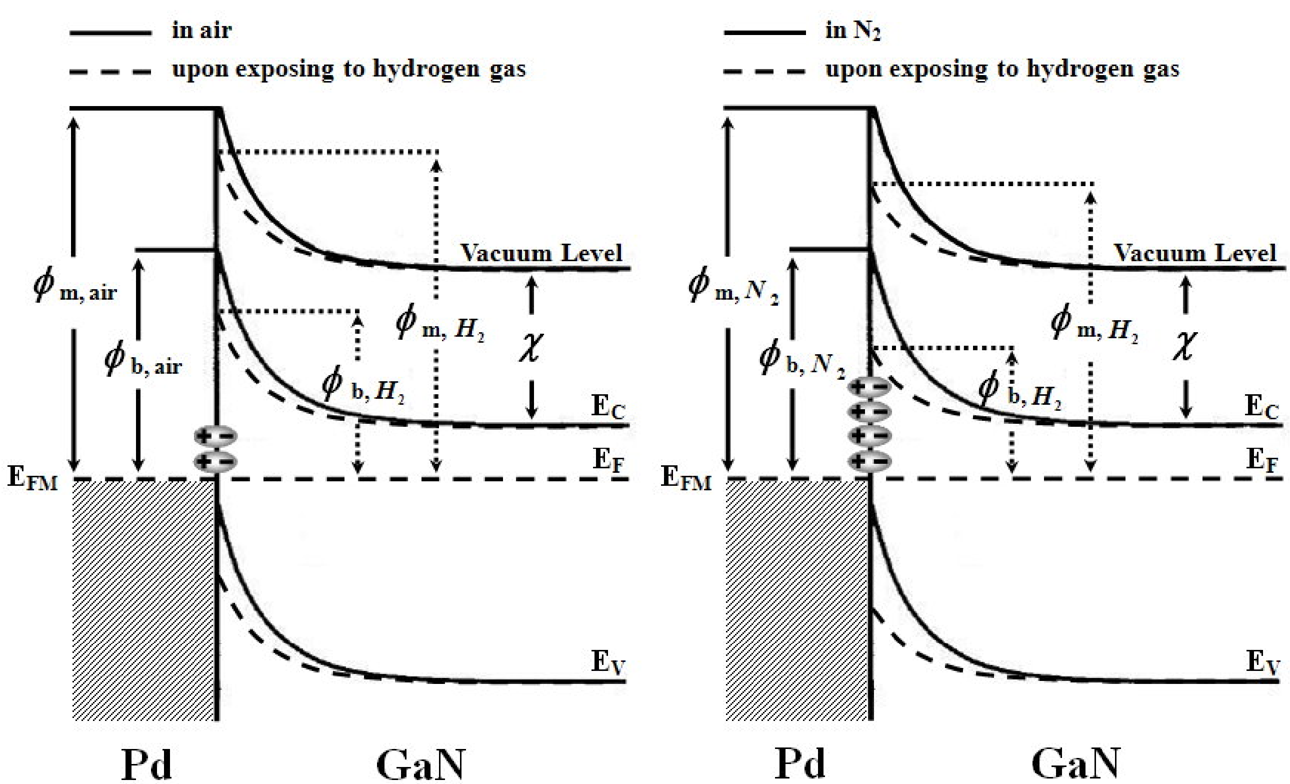


Figure 2:
The hydrogen sensing mechanism for the effectively Schottky barrier height variation.

The hydrogen sensing mechanism can be briefly elaborated as follows. When hydrogen gases are introduced, some hydrogen molecules are dissociated on the catalytic Pd metal surface and become hydrogen atoms. These hydrogen atoms are then adsorbed on the Pd metal surface, and subsequently diffuse through the thin Pd metal film until they are adsorbed at the Pd/GaN metal-semiconductor (MS) interface. The hydrogen atoms adsorbed at the MS interface become polarized and form a dipolar layer near the interface. The observed Schottky barrier height lowering phenomenon can be attributed to the appearance of this dipolar layer at the MS interface. In addition, as compared with that in N_2 atmosphere, the moderate decrease of sensing current caused by H_2 in air can be due to the competitive reactions. During the hydrogen adsorption process, the additional hydroxyl and water products are involved in the reaction upon exposing to air. The amount of H atoms dissolved at the steady state is considered to be reduced in air atmosphere due to the presence of oxygen adsorbates on the Pd surface. The reaction of water formation appears to be the rate-limiting factor and further inhibits the appearance of a dipolar layer at the interface between Pd metal and GaN. Therefore, the interfacial effect induced hydrogen leads to a larger change in the effective Schottky barrier height in N_2 atmosphere than that in air, as shown in Fig. 2. This also causes the significant magnitude of the change both in the forward- and reverse-biased currents.

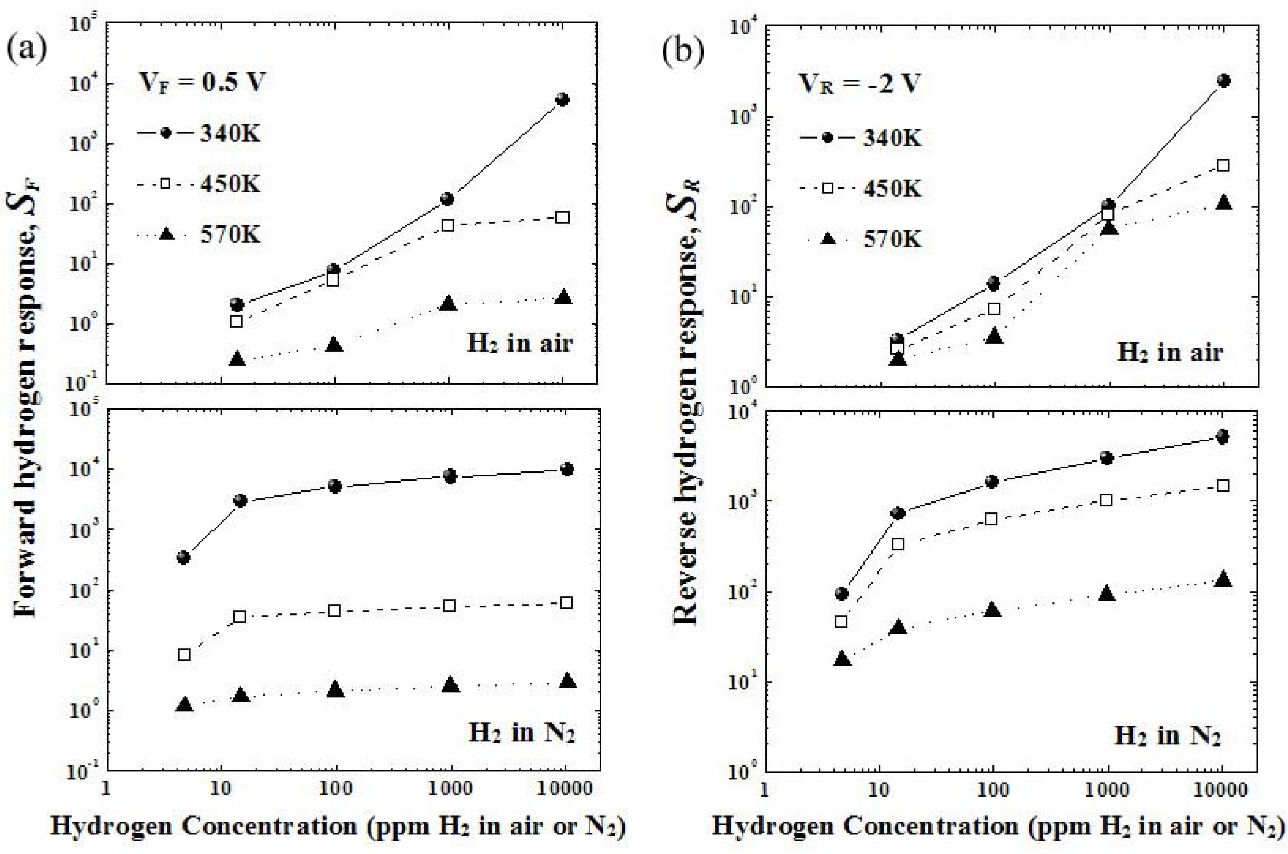


Figure 3(a) and 3(b):
The (a) forward and (b) reverse hydrogen responses when exposing to different hydrogen concentrations at 340, 450 and 570 K, respectively. The applied forward and reverse voltages are fixed at V_F = 0.5 and V_R = -2 V, respectively.

Figure 3(a) shows the forward hydrogen response and hydrogen concentration at 340, 450 and 570 K, respectively. The applied forward voltage is fixed at V_F = 0.5 V. The forward hydrogen response (S_F) is defined as:

$$S_F = \frac{I_{H_2} - I_{air}}{I_{air}} \quad (1)$$

where I_{air} and I_{H_2} are the currents measured in air and a hydrogen-containing ambience, respectively. The response variation in air atmosphere arises from two mechanisms: the I_{H_2} current induced by H_2 is attributed to the occupation of hydrogen coverage sites and the I_{air} current is based on the transport of electrons over the potential barrier. The I_{air} caused by the transport can be adequately represented by the thermionic emission current. At relatively lower temperature (340 K), the adsorption sites on the Pd/GaN interface are occupied effectively by hydrogen atoms, so that the I_{H_2} increases. In addition, the Schottky barrier height under the forward bias condition is decreased further. This behavior also results in an increase of I_{H_2}. As mentioned above, the S_F values are larger than S_R at 340 K, as shown in Fig. 3 (b). On the other hand, the coverage sites occupied by hydrogen atoms are not so effectively under a relatively high hydrogen concentration, especially at higher temperature (570 K). This phenomenon results in a decrease of I_{H_2}. Although the thermionic emission current increases with increasing the temperature, the variation of Schottky barrier height becomes relatively insignificant especially under the forward bias condition at higher temperatures. Therefore, the S_F values are relatively insignificant in comparison with S_R as the temperature is elevated to 570 K. In addition, as compared with that in air atmosphere, the magnitude of the response induced by H_2 balanced with N_2 is considered to be large under both forward and reverse bias conditions.

Based on the thermionic-emission transport mechanism, when the applied forward voltage (V) is larger than $3kT/q$, the Schottky barrier height (Φ_b) can be calculated as:

$$\phi_b = \left(\frac{kT}{q}\right) \ln\left(AA^{**}\frac{T^2}{I_0}\right) \quad (2)$$

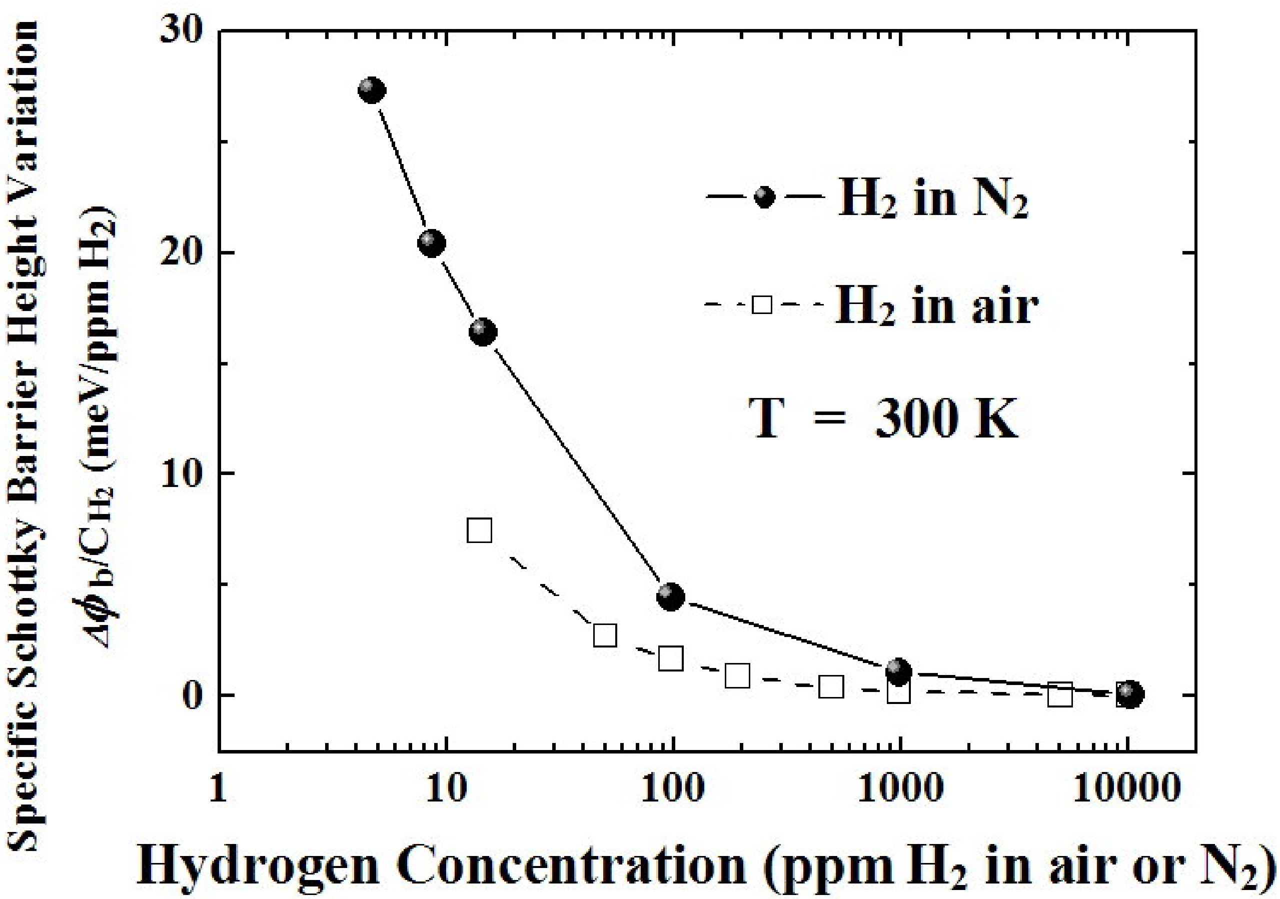


Figure 4:
The specific Schottky barrier height variation, $\Delta\phi_b$ / C_{H_2} (meV/ppm H_2), as a function of hydrogen concentration at 300 K. C_{H_2} is the introduced hydrogen concentration balanced with air or N_2.

where $\boldsymbol{k}$ is the Boltzmann constant, $\boldsymbol{T}$ the absolute temperature, $\boldsymbol{A}$ the Schottky contact area, $\boldsymbol{A^{**}}$ the effective Richardson constant (24 $Acm^{-2}K^{-2}$ for n-GaN), and $\boldsymbol{I_0}$ the saturation current. Figure 4 shows the specific Schottky barrier height variation, $\Delta\phi_b$ / C_{H_2} (meV/ppm H_2), as a function of hydrogen concentration at 300 K. C_{H_2} is the introduced hydrogen concentration balanced with air or N_2. Obviously, the $\Delta\phi_b$ / C_{H_2} value decreases with increasing the hydrogen concentration balanced with air or N_2. Due to the larger $\Delta\phi_b$ / C_{H_2} in N_2 atmosphere, the studied diode offers a higher hydrogen detection capability and a larger change in the Schottky barrier height.

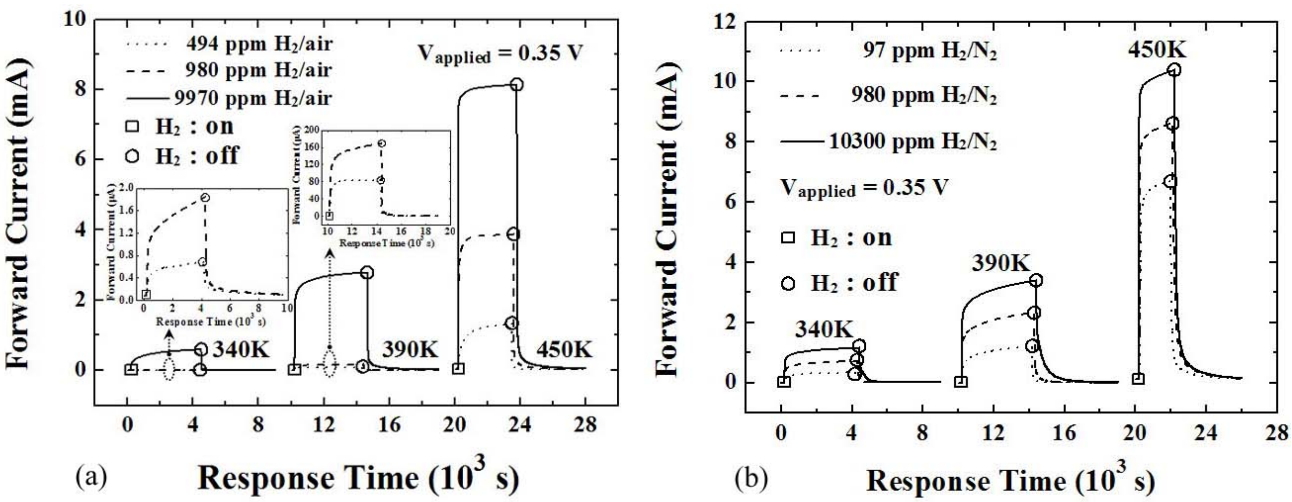


Figure 5(a) and 5(b):
The transient response curves of the studied Pd/GaN Schottky diode under the introduction and removal of different-concentration hydrogen gases of 494, 980 and 9970 ppm H2 in (a) air and (b) N_2 atmospheres at 340, 390 and 450 K. The forward bias is kept at 0.35 V.

Figure 5(a) shows the transient response curves of the studied Pd/GaN Schottky diode under the introduction and removal of different-concentration hydrogen gases of 494, 980 and 9970 ppm H_2 in air atmosphere at 340, 390 and 450 K. The forward bias is kept at 0.35 V. Clearly, the current variation is increased with an increase of the introduced hydrogen concentration. Yet, the magnitudes of the current changes are more obvious in N2 atmosphere than those in air, as shown in Fig. 5(b). Figure 6 shows the hydrogen detection adsorption time constant (τ_a) and the initial rate of change in current ($\Delta \boldsymbol{I}/\Delta \boldsymbol{t}$) ($\mu As^{-1}$) upon the switching actions as a function of temperature measured in a 980 ppm H_2 gas in air and N_2 atmospheres. Clearly, τ_a decreased with elevating the temperature. On the contrary, the corresponding $\Delta \boldsymbol{I}/\Delta \boldsymbol{t}$ increased with elevating the temperature. The hydrogen detection adsorption time constant (τ_a), defined as the time reached the inverse exponential (e^{-1}) value of the final steady-state current, decreased from 411.5 to 16 s in air atmosphere and from 95.5 to 6 s in N_2 atmosphere, respectively, as the temperature increased from 340 to 570 K. Subsequently, the corresponding $\Delta \boldsymbol{I}/\Delta \boldsymbol{t}$ values increased from 0.03 to 279.32 μAs^{-1} in air atmosphere and from 17.15 to 907.09 μAs^{-1} in N_2 atmosphere, respectively. Apparently, during the hydrogen adsorption process, the studied device demonstrates a considerably high speed and large current variation for hydrogen detection procedure at higher temperatures both in air and N_2 atmospheres, particularly above 450 K. In addition, it is known that the studied device reveals relatively smaller τ_a in N_2 atmosphere than that in air especially at lower temperatures.

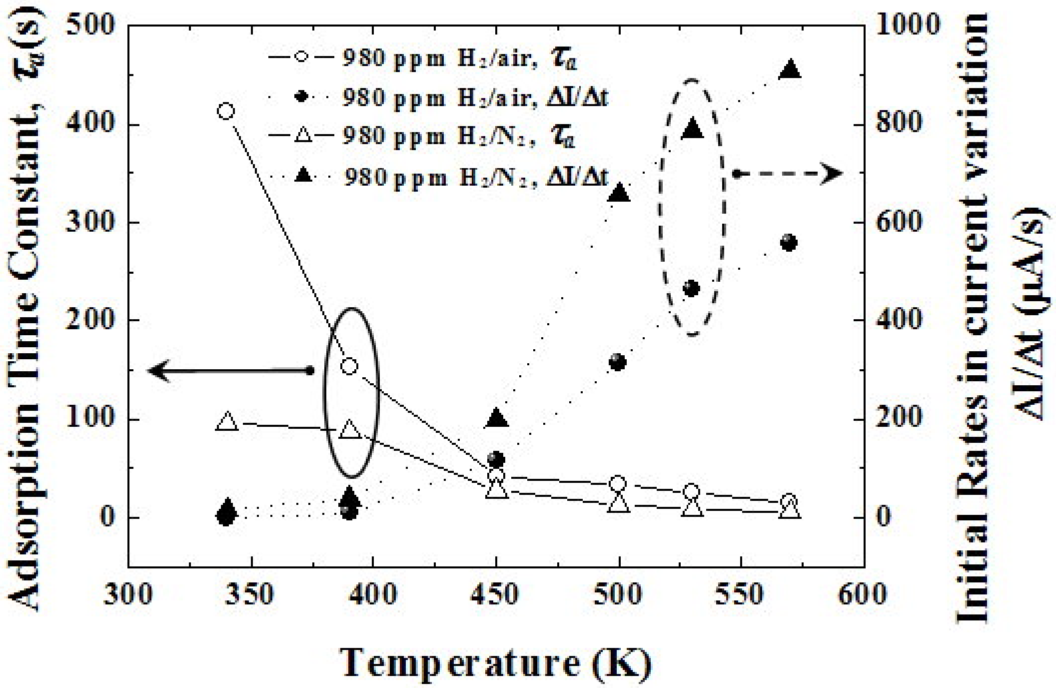


Figure 6:
The hydrogen detection adsorption time constant (τ_a) and the initial rate of change in current ($\Delta I/\Delta t$) (μAs^{-1}) upon the switching actions as a function of temperature measured in a 980 ppm H_2 gas in air and N_2 atmospheres.

4. Conclusion

The hydrogen sensing and response characteristics of a Pd/GaN Schottky diode under different-concentration hydrogen gases were studied and compared over a wide temperature range both in air and N_2 atmospheres. The studied Pd/GaN Schottky diode exhibited higher hydrogen detection capability and larger Schottky barrier height modulation in N_2 atmosphere in comparison with those in air. Furthermore, the studied device exhibited a more notable finding which showed a large and reversible response to hydrogen sensing especially at high temperatures even in N_2 atmosphere. On the other hand, the faster response in N_2 atmosphere than in air was attributed to the influence from the hydrogen molecule precursor state to the hydrogen atom chemisorbed state without oxygen adsorbates. The reaction of water formation appeared to be the rate-limiting factor and further inhibited hydrogen atoms trapped at the Pd/GaN interface during the hydrogen adsorption process in air. Therefore, based on these results, it was revealed that the studied Pd/GaN Schottky diode showed excellent hydrogen sensing performance when operated in N_2 atmosphere.