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On a GaAs-based transistor-type hydrogen sensing detector with a Pd/Al0.24Ga0.76As metal–semiconductor Schottky gate

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Abstract
An interesting transistor-type hydrogen sensing detector based on a GaAs pseudomorphic high electron mobility transistor (PHEMT) with a Pd/Al0.24Ga0.76As metal–semiconductor Schottky gate structure is fabricated and investigated. Steady-state properties and transient responses under different temperatures and hydrogen concentrations are measured and studied. Significant modulations in electrical signals are observed, obviously due to the adsorption of hydrogen atoms at the Pd–semiconductor interface. Also, the studied device exhibits fast response and recovery properties. The corresponding adsorption and desorption time constants (τa and τb) are 2.5 and 6 s, respectively, under 9970 ppm H2/air gas at 160 °C. Furthermore, based on the Langmuir isotherm and the van’t Hoff equation, a hydrogen adsorption heat of −37.02 kJ mole−1 is obtained at lower operating temperatures (≤ 72 °C). However, at a high temperature region (≥ 92 °C), the ΔH value is increased to −68.62 kJ mole−1. The hydrogen adsorption heat at lower and higher temperature regimes is demonstrated and studied. Consequentially, based on the experimental results, the studied device is promising for GaAs integrated circuit (IC) and micro electric and mechanic system (MEMS) applications.

Introduction
Hydrogen is a clean source for fuel cell and internal combustion engine applications [1, 2]. However, the widespread use of hydrogen as a fuel will require innovations in hydrogen storage and sensing. Reliable, cheap, compact and safe hydrogen sensors are required both for measuring the hydrogen concentration in flowing gas streams and for monitoring hydrogen leakage. Hydrogen-sensitive transistor-type devices [3–8] were produced and reported more than two decades ago. They are promising solid-state devices for monitoring hydrogen and hydrogen-containing gases in a wide range of commercial applications. In comparison with the conventional measuring instruments such as gas chromatography (GC), mass spectrometry (MS) and GC/MS, these devices are attractive alternatives because they exhibit the chemical specificity and high sensitivity to hydrogen gases. Also, their simple and compact structures are favourable for...
economic mass production. Another important advantage of the transistor-type hydrogen sensors is that the practical current or voltage can be easily measured with a very high precision. Moreover, the potentiality generated by these devices is relatively independent of dimensions. On the other hand, for the solid-state hydrogen sensor, catalytic effects play an important role, because the catalytic processes not only control the chemical reaction rate but also substantially affect the sensitivity and selectivity. Usually, Pd and Pt are used as the catalytic metal due to its high solubility and diffusivity [9, 10].

Over the past few years, a pseudomorphic high electron mobility transistor (PHEMT) structure, involving $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$ metal–semiconductor Schottky contact structure is fabricated and studied. Hydrogen sensing characteristics on steady-state and transient response are measured under different concentrations of hydrogen gases at different temperatures. The electrical characteristics, including drain current variation ($\Delta I_D$), output conductance ($g_{ob}$), and transconductance ($g_m$) of the studied device are dependent on hydrogen concentration and operating temperature. Based on the Langmuir isotherm and the van’t Hoff equation, the thermodynamic properties of the studied device are also investigated. Experimentally, an additional increase of hydrogen adsorption heat is obtained at high temperature regions. This phenomenon can be related to different physical mechanisms. One is the original adsorption of hydrogen atoms at a metal–semiconductor interface. This creates a dipolar layer. Another mechanism is the donor neutralization. The diffusing hydrogen atoms will be trapped by Si dopants in the AlGaAs Schottky contact layer.

**Experimental details**

The studied GaAs-based PHEMT hydrogen sensor was grown by a low-pressure metal organic chemical vapour deposition (LP-MOCVD) system on a (1 0 0) oriented semi-insulated (SI) GaAs substrate. The detailed epitaxial structure consisted of a 5000 Å thick GaAs undoped buffer layer, a 150 Å thick undoped In$_{0.15}$Ga$_{0.85}$As channel, a 45 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As spacer, a 45 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As Schottky contact layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer, a 4 Å thick undoped Al$_{0.24}$Ga$_{0.76}$As cap layer. Silane (SiH$_4$) was used as the n-type dopant. After epitaxial growth, the studied device was fabricated by using conventional photolithography, wet chemical etching, vacuum evaporation, lift-off and rapid thermal annealing (RTA) techniques. Mesa etching was first employed to etch the samples into the substrate with an H$_3$PO$_4$:H$_2$O$_2$:H$_2$O (1:1:20) solution at room temperature to isolate the devices. Then, the drain-source ohmic contacts were formed by evaporating Au/Ge/Ni metals on the n$^+$-GaAs cap layer and alloying in nitrogen gas at 380 °C for 20 s. The chemically etched surfaces were prepared by removing the native oxide with a solution of HF:H$_2$O = 1:1. Finally, the gate Schottky contacts with a gate length of 1.4 μm were achieved by depositing the catalytic Pd metal on the Al$_{0.24}$Ga$_{0.76}$As Schottky contact layer. Figure 1 illustrates the sputter Auger electron spectroscopy (AES) depth profiles of the studied Pd/Al$_{0.24}$Ga$_{0.76}$As HEMT device. Due to the inherent property of AlGaAs material, it is easy to form a native oxide layer on the surface. Yet, as shown in figure 1, the insignificant signal of O element is observed. This confirms that the native oxide layer presented at the Pd metal and the Al$_{0.24}$Ga$_{0.76}$As layer interface is negligible. The schematic cross section of the studied device is also depicted in the inset of figure 1.

**Results and discussion**

Figures 2(a) and (b) are the typical three-terminal output current–voltage (I–V) characteristics under different concentrations of hydrogen gases at 30 and 160 °C, respectively. The hydrogen atoms diffuse into the catalytic Pd metal and are adsorbed at the metal–semiconductor interface. Clearly, changes of sensing signals with different hydrogen concentrations are obtained. This means that those dipolar moments cause the substantial current variations. As shown in figure 2(a), even at an extremely low-hydrogen concentration of 4.3 ppm H$_2$/air, significant current variation can be found. A high magnitude of 6.0 mA in drain current variation is obtained under 9970 ppm H$_2$/air gas at the fixed voltages of $V_{GS} = 0$ V and $V_{DS} = 1.5$ V. However, while the temperature is increased to 160 °C (as shown in figure 2(b)), the lowest
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Figure 2. Common-source output current–voltage (I–V) characteristics of the studied device under different concentrations of hydrogen gases at (a) 30 °C and (b) 160 °C, respectively.

detection limit of hydrogen concentration is increased to 494 ppm H2/air. Also, the corresponding current variation is decreased from 46.5 to 0.22 mA (at 160 °C). This phenomenon can be attributed to the exothermic reactions during the hydrogen adsorption process. Figure 3(a) shows the drain current variation $\Delta I_D$ as a function of the hydrogen partial pressure $P_{H2}$ at different temperatures. $\Delta I_D$ at lower temperature is considerably larger than that at higher temperature. With the increase of hydrogen partial pressure, the corresponding $\Delta I_D$ values are increased. This causes more hydrogen atoms to be absorbed at the Pd–semiconductor interface. In order to study the detection capability of hydrogen, a drain current sensitivity $S_I$ is defined as

$$S_I = \frac{(I_{D,H2} - I_{D,air})}{C_{H2}} \left( \mu\text{A/ppm H}_2 \right),$$

where $I_{D,H2}$ and $I_{D,air}$ are the drain currents measured under hydrogen-contained ambience and air, respectively and $C_{H2}$ is the introduced hydrogen concentration. The relationships between the drain current sensitivity $S_I$ and temperature under different concentrations of hydrogen gases are shown in figure 3(b). The applied voltages are fixed at $V_{GS} = 0$ V and $V_{DS} = 1.5$ V. It is obvious that the $S_I$ value is decreased with the increase of temperature and hydrogen concentration. For example, on exposing to 98 ppm H2/air gas, the corresponding $S_I$ value is decreased from 46.5 ppm H2/air.

Figure 3. (a) The drain current variation $\Delta I_D$ as a function of the hydrogen partial pressure $P_{H2}$ at different temperatures. (b) Drain current sensitivity $S_I$ versus temperature under 98, 980 and 9970 ppm H2/air gases.
to 1.1 μA/ppm H₂, as the temperature is increased from room temperature to 132 °C. Also, at higher temperatures, a relatively drastic decrease of S₁ values is observed. This may be attributed to the consumption of a large number of adsorbed hydrogen atoms during the surface chemical reactions at higher temperature. Figure 4 shows the transconductance g_m, output conductance g_ds and voltage gain A_v versus drain-source voltage V_DS under different concentrations of hydrogen gases at room temperature. Obviously, hydrogen concentration-dependent transistor amplification behaviours are found. Under the bias condition of V_DS = −0.3 V and V_DS ≥ 1.0 V, the g_ds/g_m value is increased from 128 (1.1) to 220 (5.1) mS mm⁻¹ under air and hydrogen-containing ambience from 98 to 9970 ppm H₂/air gas. The corresponding A_v(g_m/g_ds) is decreased from 116.4 (in air) to 43.1 (under 9970 ppm H₂/air gas).

It is known that the hydrogen sensing ability is dependent on the properties of the hydrogen adsorption states at the Pd–semiconductor interface, such as adsorption heat, site density and polarizability [19]. Generally, hydrogen gas dissociates on a Pd surface very effectively, often with a relatively higher coefficient. The transient time across the Pd film, in the order of 10⁻⁵ s, is substantially lower than the time of occupation on the surface (about 1 s) [20]. In other words, the rate determining barrier between the adsorption state and Pd bulk state is negligible. The adsorption of hydrogen can be described as

\[ \frac{1}{2} H_2(g) \rightleftharpoons c \xrightarrow{d} H_{(s)} \xleftarrow{c} H_{(a)} \xrightarrow{d} H_{(i)}. \]  

The subscripts g, s, b and i denote gas phase, Pd metal surface, Pd metal bulk and Pd–semiconductor interfacial state, respectively. c and d are the forward and reverse diffusing rate constants in Pd metal bulk. c₁(c₂) and d₁(d₂) are rate constants for forward and reverse reactions in surface adsorption (in interfacial adsorption), respectively. According to the Langmuir-type model, the equilibrium constant K_e of overall adsorption reaction can be represented in terms of the hydrogen pressure P_H₂ and the interfacial hydrogen coverage θ_H \_i [18, 21]:

\[ K_e = \frac{c_1 \cdot c_2}{d_1 \cdot d_2} = \frac{\theta_H}{P_H^0(1 - \theta_H)}, \]  

where θ_H \_i is varied from 0 to 1. Not only the change of interface coverage, but also the threshold voltage shifts are caused by the adsorption of hydrogen atoms at the metal–semiconductor interface. Therefore, the changes in the threshold voltage ΔV_th can be considered as proportional to the hydrogen coverage [22]:

\[ \Delta V_{th} = V_{th,air} - V_{th,H_2} = \Delta V_{th,max} \cdot \theta_H, \]  

where V_{th,air} and V_{th,H_2} are the threshold voltages measured at air and hydrogen-contained ambience, respectively and ΔV_{th,max} is the maximum shift of the threshold voltage. By combining equations (3) and (4), the Langmuir isotherm equation can be rewritten as

\[ \frac{1}{\Delta V_{th}} = \frac{1}{\Delta V_{th,max}} \left( \frac{K_e \cdot P_H^{-0.5}}{\Delta V_{th,max}} \right) + \frac{1}{\Delta V_{th,max}}. \]  

The linear relationships between the inverse square root of hydrogen partial pressure P_H₂^{-0.5} and the inverse threshold voltage shift 1/ΔV_{th} of the studied device at 30, 52 and 72 °C are plotted in figure 5(a). The corresponding characteristics at 92, 112 and 132 °C are shown in figure 5(b). This linearity confirms that the experimental data are consistent with the theoretical analysis. Furthermore, the equilibrium constant K_e can be obtained from figures 5(a) and (b). The K_e value is decreased from 1.77 to 0.16 as the temperature is increased from 30 to 132 °C. Since the hydrogen adsorption process is exothermic, the K_e values are decreased with increasing temperature.

On the other hand, based on the thermodynamic relation, the temperature-dependence on the K_e value can be expressed as [23]

\[ \ln K_e = \frac{-\Delta H^0}{R} \frac{\Delta S^0}{R}, \]  

where ΔH^0 and ΔS^0 are the enthalpy change and entropy change, respectively. Figure 6 illustrates the logarithmic value of equilibrium constant ln K_e versus inverse absolute temperature 1000/T. It is interesting to note that at a lower temperature region (from 30 to 72 °C) the smaller ΔH^0 value of −37.02 kJ mole⁻¹ is obtained. However, as the temperature is increased to a higher temperature region (from 92 to 132 °C), the corresponding ΔH^0 value is decreased as −68.62 kJ mole⁻¹. Clearly, these phenomena are related to different physical mechanisms. One is the original adsorption of hydrogen atoms at the metal–semiconductor interface. This creates a dipolar layer. Another mechanism may be the donor neutralization [24]. The diffused hydrogen atoms can be trapped by Si dopants in the n-type AlGaAs Schottky contact layer [24], because Si is used as n-type dopants during the epitaxial process. On the other hand, the dissociated hydrogen atoms are not only trapped at the Pd–semiconductor interface, but also diffuse into the semiconductor [25]. Thus, those hydrogen atoms diffusing into the semiconductor are associated with Si dopant atoms, which results in the Si–H entities [26]. These dependences of hydrogen solubility and diffusivity on the impurity and defect concentrations were
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observed in metals and amorphous silicon [27, 28]. Generally, based on the Langmuir isotherm analysis, the hydrogen adsorption heat at all operating temperatures is kept constant. Thus, at a lower temperature region, the formation of a dipolar layer will dominate the whole hydrogen adsorption process due to the weak and negligible effect of Si donor neutralization at low temperature [29]. Experimentally, the adsorption heat of $-37.02 \text{ kJ mole}^{-1}$ is obtained from the hydrogen adsorption at the metal–semiconductor interface. However, at the high temperature region ($\geq 92 ^\circ \text{C}$), the total hydrogen adsorption heat is about $-68.62 \text{ kJ mole}^{-1}$. The additional decrease of hydrogen adsorption heat of 31.6 kJ mole$^{-1}$ may be caused by the reactions between diffused hydrogen atoms and Si dopant atoms. In other words, both hydrogen sensing and donor neutralization mechanisms are simultaneously presented in a high temperature region. Figure 7(a) shows the maximum threshold voltage shift $\Delta V_{th,max}$ as a function of temperature. Obviously, at a lower temperature region ($\leq 92 ^\circ \text{C}$), the $\Delta V_{th,max}$ value is decreased with increasing temperature. Then, an inverse tendency is observed while the temperature is increased over 92 $^\circ \text{C}$. This may be caused by the formation of Si–H complexes due to the activation of Si dopant atoms by the increase of temperature [26]. However, as seen in figure 7(b), the magnitude of the threshold voltage shift $\Delta V_{th}$ is still decreased even though $\Delta V_{th,max}$ is increased. This is attributed to the decrease of diffused hydrogen atoms resulting from the adsorption competition and oxygenated reaction between hydrogen and oxygen gases on the Pd surface at higher temperature ($\geq 92 ^\circ \text{C}$) [30]. In other words, the number of diffused hydrogen atoms is determined by surface reactions.

The typical hydrogen current–response curves upon the introduction and the removal of 9970 ppm H$_2$/air gas at different temperatures are shown in figure 8. The applied voltages are kept as $V_{GS} = -0.3 \text{ V}$ and $V_{DS} = 1.2 \text{ V}$. The characteristic modulations under hydrogen exposure are caused by the change of gate built-in potential resulting from the accumulation effect of atomic hydrogen at the gate metal/semiconductor interface. This causes a decrease in gate built-in potential, and therefore an increase in current. Since the diffusion coefficient for hydrogen in Pd is fairly large [9], the equilibrium between the adsorbed and the absorbed amount will be rapidly established. This also implies that any adsorption state on the internal Pd surface will also be in equilibrium with the adsorption states on the external surface. However, as the temperature is increased over 112 $^\circ \text{C}$, an
over-shoot phenomenon is observed [31–33]. This may be attributed to the consumption of adsorbed hydrogen atoms by the adsorbed oxygen in the form of hydroxyl species or water on the Pd metal surface [30]. In other words, the interfacial coverage sites occupied by hydrogen atoms are decreased due to the existence of adsorbed oxygen atoms on the Pd surface. Thus, the surface reaction dominates the number of diffused hydrogen atoms, especially at higher temperature. Figure 9 shows the response and recovery time constants (\(\tau_a\) and \(\tau_b\)) as a function of temperature under 9970 ppm H\(_2\)/air gas. The applied voltages are kept at \(V_{GS} = -0.3\) V and \(V_{DS} = 1.2\) V.

Figure 7. (a) The relationship between the maximum threshold voltage shift \(\Delta V_{th,\text{max}}\) and the operating temperature. (b) The threshold voltage shift \(\Delta V_{th}\) as a function of temperature under 9970 ppm H\(_2\)/air gas.

Figure 8. Hydrogen current–response curves of the studied device upon the introduction and removal of 9970 ppm H\(_2\)/air gas. The applied voltages are kept at \(V_{GS} = -0.3\) V and \(V_{DS} = 1.2\) V.

Figure 9. Response and recovery time constants (\(\tau_a\) and \(\tau_b\)) of the studied device versus temperature under 9970 ppm H\(_2\)/air gas.
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number of interfacial coverage sites and the higher reaction rate induced by more collisions and chemistry on the Pd metal surface.

Conclusion

In summary, an interesting transistor-type hydrogen sensing detector based on GaAs PHEMT with a Pd/Al0.24Ga0.76As metal–semiconductor Schottky gate structure is fabricated and studied. Even at an extremely low-hydrogen concentration of 4.3 ppm H₂/air, significant current variation can be found. On exposing to 98 ppm H₂/air gas, the corresponding sensitivity Sₐ is decreased from 46.5 to 1.1 μA/ppm H₂, as the temperature is increased from room temperature to 132 °C. Based on the Langmuir isotherm and the van’t Hoff equation, a hydrogen adsorption heat of −37.02 kJ mole⁻¹ is obtained. However, at a high temperature region, the ΔH⁰ value is increased to −68.62 kJ mole⁻¹. This additional increase of the ΔH⁰ value (31.6 kJ mole⁻¹) may be caused by a different mechanism of Si donor neutralization. In transient response analysis, the fast response and recovery of the studied device can be obtained under different concentrations of hydrogen gases at different temperatures. The corresponding adsorption and desorption time constants (τₐ and τₜₙ) are 2.5 and 6 s, respectively, under 9970 ppm H₂/air gas at 160 °C. Consequently, based on the good experimental results, the studied PHEMT hydrogen detector is promising for GaAs integrated circuit (IC) and micro electric and mechanic system (MEMS) applications.

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