



Devices based on series-connected Schottky junctions and β -Ga₂O₃/SiC heterojunctions characterized as hydrogen sensors

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Abstract. Field-effect hydrogen gas sensor devices were fabricated with the structure of a series connection between Schottky junctions and β -Ga₂O₃/6H-SiC heterojunctions. β -Ga₂O₃ thin films were deposited on n-type and p-type 6H-SiC substrates by gallium evaporation in oxygen plasma. These devices have rectifying properties and were characterized as hydrogen sensors by a Pt electrode. The hydrogen-sensing properties of both devices were measured in the range of 300–500 °C. The Pt/Ga₂O₃/n-SiC device revealed hydrogen-sensing properties as conventional Schottky diode-type devices. The forward current of the Pt/Ga₂O₃/p-SiC device was significantly increased under exposure to hydrogen. The behaviors of hydrogen sensing of the devices were explained using band diagrams of the Pt/Ga₂O₃/SiC structure biased in the forward and reverse directions.

1 Introduction

Hydrogen gas has been expected to be employed as a clean energy source for various applications. For example, fuel cells will be used to power vehicles and as domestic and industrial energy systems in the near future. However, because the explosion limit of hydrogen gas is 4 % in air, quick detection of low hydrogen concentration is required to avoid a dangerous situation. Therefore, small, inexpensive hydrogen sensors would be required to ensure safety standards.

Many researchers have studied several types of hydrogen sensor devices with sintered metal oxide thin films formed by means of various methods that are based on the field effect.

β -Ga₂O₃ is a semiconductor material with a wide band gap of 4.9 eV and has been in focus as a new material for solar-blind deep UV detectors (Kokubun et al., 2007; Suzuki et al., 2009; Nakagomi et al., 2013b) and power devices (Higashiwaki et al., 2012).

Many Ga₂O₃-based gas sensors have also been investigated. Fleischer and Meixner (1991) studied an oxygen sensor with a Ga₂O₃ film prepared by sputtering that could be applied at temperatures over 500 °C. The sensor was also sensitive to reducing gases such as hydrogen (Fleischer and Meixner, 1992; Fleischer et al., 1992). Ogita et al. (1999) also

fabricated an oxygen gas sensor based on Ga₂O₃ prepared by sputtering that exhibited dependence on the oxygen pressure used during the sputtering process. Trinchi et al. (2004) proposed a sensor device with a Pt/Ga₂O₃/SiC structure for the first time. A Ga₂O₃ layer was formed on an n-type SiC substrate using a sol-gel method. They demonstrated hydrogen-sensing properties due to a change in the Schottky barrier height. However, the sensor characteristics were measured only under forward bias conditions, and the current–voltage (I – V) characteristics were not examined in detail. The authors have inferred from the I – V characteristics presented by Trinchi et al. (2004) that the Ga₂O₃ layer acts as an electrical resistance layer because the change in the I – V characteristics caused by a change in the atmosphere is not just a simple shift in the turn-on voltage but in fact includes a change in slope. This indicates a change in the resistance component of the Ga₂O₃ layer.

We have previously reported the first hydrogen sensor with a Schottky diode structure based on a Ga₂O₃ single crystal (Nakagomi et al., 2011a, b). In addition, we have also reported field-effect hydrogen gas sensor devices based on β -Ga₂O₃ thin film formed on a sapphire substrate (Nakagomi et al., 2013a).

6H-SiC and 4H-SiC are well-known semiconductor materials for high-power applications with wide band gaps of 3.02 and 3.26 eV, respectively. Gas sensor devices based on SiC that can be operated at higher temperatures have also been reported (Spetz et al., 2004).

In this study, field-effect hydrogen gas sensor devices with a series connection between Schottky junctions and β -Ga₂O₃/6H-SiC heterojunctions were fabricated. β -Ga₂O₃ thin films were deposited on n-type and p-type 6H-SiC substrates, and the hydrogen sensitivities of the Pt/Ga₂O₃/n-type SiC and Pt/Ga₂O₃/p-type SiC structures were evaluated in detail. Both devices exhibited rectifying and hydrogen-sensing properties dependent on the bias conditions.

2 Experimental

2.1 Preparation of β -Ga₂O₃ thin film

The β -Ga₂O₃ layer was prepared using gallium evaporation in oxygen plasma. After the SiC substrate was heated to 800 °C, 4 mL min⁻¹ of O₂ was supplied into the vacuum chamber to form oxygen plasma at 100 W RF power. The pressure of the chamber at that time was about 5×10^{-4} Torr. Gallium was thermally evaporated using a crucible in the chamber. Then the β -Ga₂O₃ thin film was formed on the SiC substrate. The preparation and crystal orientation of β -Ga₂O₃ layers on sapphire substrates with this method have been previously reported (Nakagomi and Kokubun, 2013). We prepared the Ga₂O₃ layer on a (001) *c*-plane 6H-SiC substrate using the same method as in the case of sapphire substrates and then evaluated the Ga₂O₃ layer. From the measurement of the X-ray diffraction pattern of the Ga₂O₃ layer, the estimated peak from β -Ga₂O₃ (111) was observed. This indicated that the Ga₂O₃ layer formed on the 6H-SiC substrate is β -Ga₂O₃. Additionally, several crystal grains were observed in a cross-sectional TEM image of the Ga₂O₃ layer. We think that the β -Ga₂O₃ layer included several crystal orientations.

2.2 Fabrication of device structures

Two types of sensor devices, shown in Fig. 1, were fabricated. One device consisted of a β -Ga₂O₃ layer deposited on an n-type 6H-SiC substrate with a resistivity of 0.09 Ω cm. As an ohmic electrode for n-type SiC, Ni (100 nm)/Ti (30 nm)/Pt (100 nm) layers were evaporated successively onto the substrate, followed by annealing at 1000 °C for 2 min in nitrogen. The other device consisted of a β -Ga₂O₃ layer deposited on a p-type 6H-SiC substrate with a resistivity of 2.2 Ω cm. As an ohmic electrode, Al (10 nm)/Ti (20 nm)/Al (100 nm)/Pt (100 nm) layers were evaporated successively onto the p-type 6H-SiC substrate, followed by annealing at 1000 °C for 2 min in nitrogen. A thin Pt layer (30 nm) with a diameter of ca. 1 mm was evaporated onto the β -Ga₂O₃ layer through a metal mask as a Schottky electrode. In this study,

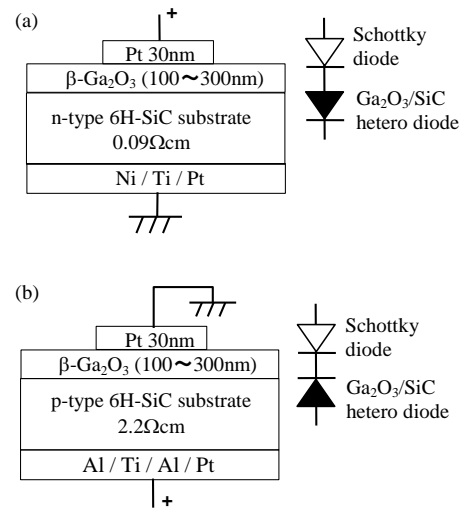


Figure 1. (a) Schematic diagram of a hydrogen gas sensor device based on the Pt/Ga₂O₃/n-SiC structure. A positive Pt electrode is referred to as forward bias. (b) Schematic diagram of a hydrogen gas sensor device based on the Pt/Ga₂O₃/p-SiC structure. A positive p-type SiC layer is referred to as forward bias.

forward bias is where the n-type SiC is biased negatively or when the p-type SiC is biased positively. The device based on the Pt/Ga₂O₃/n-SiC structure corresponds to a series connection between a Schottky diode and a Ga₂O₃/SiC heterojunction diode in the same direction. The device based on the Pt/Ga₂O₃/p-SiC structure corresponds to a series connection between a Schottky diode and a Ga₂O₃/SiC heterojunction diode in opposite directions to each other.

2.3 Device evaluation

A sensor device was placed in a quartz tube furnace with a thermocouple to monitor the temperature. The temperature of the device was controlled for measurements at 300, 400 and 500 °C. SiC and β -Ga₂O₃ are well known as wide band gap semiconductors; therefore, these devices based on β -Ga₂O₃ and SiC can operate at higher temperatures.

A mixed gas of N₂, O₂, H₂ and 1% H₂/N₂ set using mass-flow controllers was supplied into the 25 mm diameter quartz tube. Oxygen and hydrogen concentrations were determined by means of a control flow rate for each gas. The total flow rate was maintained at 500 mL min⁻¹ for all measurements. The *I*-*V* characteristics were measured in 20% O₂/N₂ and 200 ppm H₂/N₂ atmospheres at 300, 400 and 500 °C using a source meter (Keithley 2400). A constant current source and digital recorder were used to measure hydrogen response curves. The hydrogen concentration was intermittently increased from 40 to 10000 ppm in the 20% O₂/N₂ atmosphere at 5 min intervals.

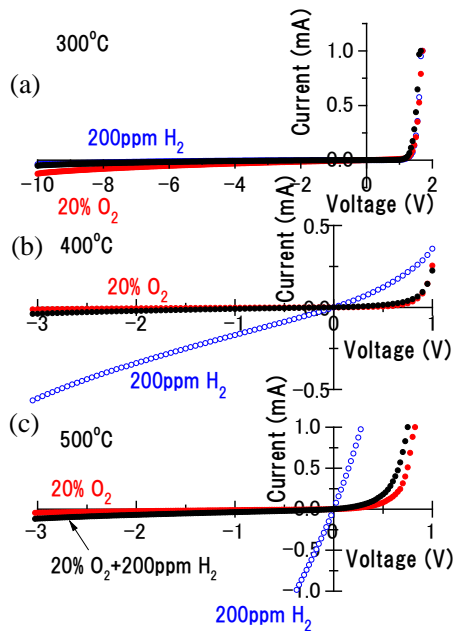


Figure 2. *I-V* characteristics of Pt/Ga₂O₃/n-SiC device in 20% O₂ / N₂, 200 ppm H₂ / N₂ and 20% O₂ + 200 ppm H₂ in N₂ measured at (a) 300, (b) 400 and (c) 500 °C.

3 Results and discussion

3.1 *I-V* characteristics

3.1.1 Pt/Ga₂O₃/n-type SiC heterojunction device

The *I-V* characteristics of the Pt/Ga₂O₃/n-SiC device measured in 20% O₂ / N₂, 200 ppm H₂ / N₂ and 20% O₂ + 200 ppm H₂ in N₂ at 300, 400 and 500 °C are shown in Fig. 2a–c. The *I-V* characteristics indicate rectifying properties at 300 °C. The current of the Pt/Ga₂O₃/n-SiC device increases when the n-type SiC is negatively biased. There was little difference in the *I-V* characteristics measured for three atmospheres at 300 °C. However, the current was increased in 200 ppm H₂ / N₂ compared with that in 20% O₂ / N₂ at 400 and 500 °C. In particular, the *I-V* characteristics in 200 ppm H₂ / N₂ were almost linear at 500 °C, which indicated a resistance without rectifying properties. A decrease in turn-on voltage in forward bias region and an increase in reverse current were observed at 500 °C.

Figure 3 shows dependence of the *I-V* characteristics of the Pt/Ga₂O₃/n-SiC device on hydrogen concentration under 20% O₂ in N₂ at 500 °C. *I-V* characteristics in 200 ppm H₂ / N₂ are also shown. With an increase in H₂ concentration, the turn-on voltage decreased in the forward bias region and the current was increased in the reverse bias region. The dependence of the *I-V* characteristics on hydrogen concentration indicates that the Pt/Ga₂O₃/n-SiC device structure can be used as a hydrogen sensor both under reverse and forward bias conditions. The *I-V* characteristics

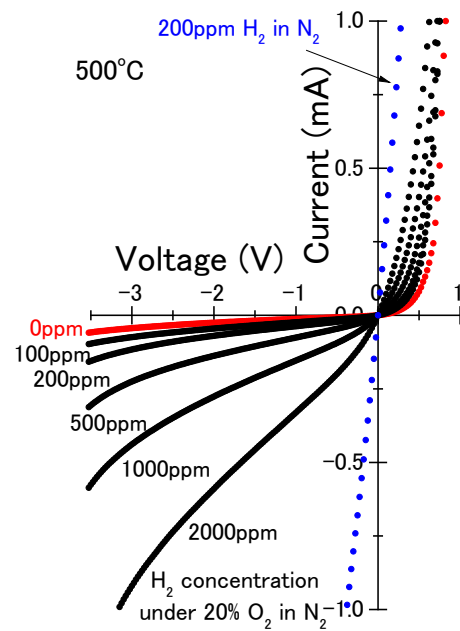


Figure 3. Dependence of *I-V* characteristics of a Pt/Ga₂O₃/n-SiC device on H₂ concentration under 20% O₂ atmosphere at 500 °C. *I-V* characteristics in 200 ppm H₂ / N₂ are also shown.

are similar to the behavior in a conventional gas sensor device with a Schottky diode structure. We have reported on a hydrogen gas sensor with a Schottky diode structure fabricated using a β -Ga₂O₃ single-crystal substrate (Nakagomi et al., 2011b). The dependence of *I-V* characteristics on hydrogen concentration is similar to the characteristics of the Pt/Ga₂O₃/n-SiC device shown in Fig. 3. In other words, the Pt/Ga₂O₃/n-SiC device reveals similar properties to conventional Schottky diode-type devices.

3.1.2 Pt/Ga₂O₃/p-type SiC heterojunction device

The *I-V* characteristics of the Pt/Ga₂O₃/p-SiC device measured in 20% O₂ / N₂, 200 ppm H₂ / N₂ and 20% O₂ + 200 ppm H₂ in N₂ at 300, 400 and 500 °C are shown in Fig. 4a–c. The *I-V* characteristics show that good rectifying properties were maintained at all measurement temperatures. The current of the Pt/Ga₂O₃/p-SiC device increased when the p-SiC substrate was positively biased. In contrast, little reverse current of the device flowed even at 500 °C. There was little difference in the *I-V* characteristics measured in the 20% O₂ / N₂ and 200 ppm H₂ / N₂ atmospheres under reverse bias conditions. In contrast, the current under forward bias was changed according to the 200 ppm H₂ / N₂, 20% O₂ + 200 ppm H₂ in N₂ or 20% O₂ / N₂ atmosphere. The forward current in 200 ppm H₂ / N₂ was significantly increased with increasing temperature, and the change in the *I-V* characteristics caused by the change in atmosphere was increased. The voltage difference under constant current in the forward bias region can be used as a sensing signal; therefore,

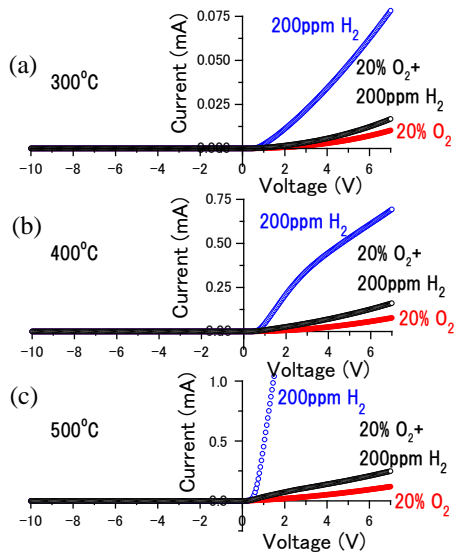


Figure 4. I – V characteristics of Pt/Ga₂O₃/p-SiC device in 20% O₂/N₂, 200 ppm H₂/N₂ and 20% O₂+200 ppm H₂ in N₂ measured at (a) 300, (b) 400 and (c) 500 °C.

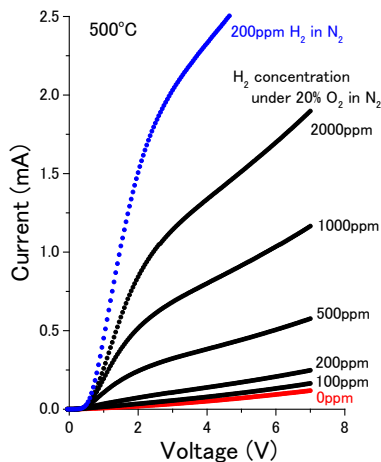


Figure 5. Dependence of I – V characteristics of Pt/Ga₂O₃/p-SiC device on H₂ concentration under 20% O₂ atmosphere at 500 °C. I – V characteristics in 200ppm H₂/N₂ are also shown.

the Pt/Ga₂O₃/p-SiC heterojunction structure is considered to be a feasible hydrogen sensor device with a large response under forward bias conditions.

Figure 5 shows dependence of the forward I – V characteristics of the Pt/Ga₂O₃/p-SiC device on hydrogen concentration under 20% O₂ in N₂ at 500 °C. I – V characteristics in 200 ppm H₂/N₂ are also shown. In 20% O₂ atmosphere without hydrogen, the forward current was low. The forward current increased with increasing hydrogen concentration. The current was more increased in 200 ppm H₂ in a N₂ atmosphere without O₂. In the conditions of higher hydrogen concentration than 500 ppm, the rate of current increase

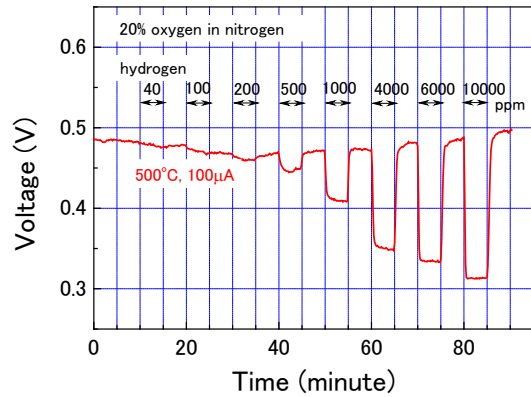


Figure 6. Response voltage curves for the Pt/Ga₂O₃/n-SiC gas sensor device with intermittent increases in the H₂ concentration in a 20% O₂/N₂ atmosphere at 500 °C. The forward bias current of the device was kept at 100 μA.

for voltage was decreased at the higher voltage than around 2–3 V. This suggests that the hydrogen-sensing mechanism of the gas sensor device with the Pt/Ga₂O₃/p-SiC structure does not proceed from a simple change in electrical resistance. The mechanism will be discussed in a later section (Sect. 4.3).

3.2 Response to hydrogen gas

3.2.1 Pt/Ga₂O₃/n-type SiC heterojunction device

Response curves of the sensor devices were measured to investigate the hydrogen gas sensitivity, response time and recovery time. Figure 6 shows voltage response curves for the Pt/Ga₂O₃/n-SiC structure device under constant current (100 μA) at 500 °C where the device was biased in the forward direction. The H₂ concentration was intermittently increased from 40 to 10 000 ppm in the 20% O₂/N₂ atmosphere. The voltage changed with an increase in the H₂ concentration, except for hydrogen concentrations lower than 200 ppm. A sharp change in the voltage was observed in the region of 500–10 000 ppm H₂. The response and recovery were almost completed within a few seconds. The results demonstrate that the sensor device can detect almost 500 ppm H₂ gas in air. Despite the very small response voltage of less than 0.2 V and the higher sensing limit of 500 ppm, the Pt/Ga₂O₃/n-SiC device structure under forward bias demonstrated a quick response and recovery.

When the Pt/Ga₂O₃/n-SiC structure was biased in reverse, the device could detect lower hydrogen concentrations and give a larger voltage response than when forward biased. Figure 7 shows voltage response curves for the device under constant current (50 μA) at 300, 400 and 500 °C. The device was able to detect 40 ppm hydrogen gas in 20% O₂. The behavior at 500 °C was remarkable. The change in voltage amounted to 5 V for 4000 ppm hydrogen, whereas the

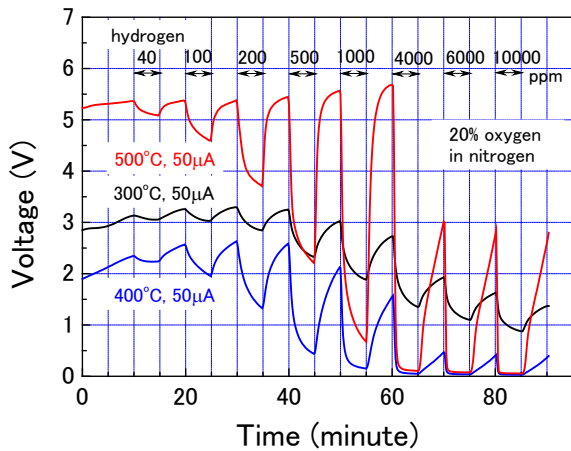


Figure 7. Response voltage curves for the Pt/Ga₂O₃/n-SiC gas sensor device with intermittent increases in the H₂ concentration in a 20% O₂ / N₂ atmosphere at 300, 400 and 500 °C. The reverse bias current of the device was kept at 50 μA.

voltage reached almost zero for the hydrogen concentrations higher than 4000 ppm. Although the response time for hydrogen concentrations higher than 4000 ppm was within a few seconds, the recovery time became slower than that when forward biased.

In the measurements of the response curve shown in Figs. 6 and 7, the temperature of the device rose and fell by around 1 °C for each temperature condition at intervals of about 10 min. These temperature fluctuations did not have a large influence on the response of the device.

3.2.2 Pt/Ga₂O₃/p-type SiC heterojunction device

The Pt/Ga₂O₃/p-SiC structure device is not very sensitive to hydrogen gas in the reverse bias condition; therefore, response curves were measured only for the forward bias condition. Figure 8 shows voltage response curves for the Pt/Ga₂O₃/p-SiC structure device under constant current (50 μA) at 300, 400, and 500 °C with forward bias. The device could detect 40 ppm hydrogen gas in 20% O₂ / N₂ when forward biased. At 300 °C, the change in voltage due to the change in hydrogen concentration was small and gradual. However, an increase in temperature resulted in an increased voltage response that amounted to 8 V for 4000 ppm hydrogen in 20% O₂ / N₂ at 500 °C. The voltage for hydrogen concentrations higher than 4000 ppm was almost 1 V. The sensor could detect 40 ppm hydrogen in 20% O₂ / N₂ at 500 °C distinctly. Although the response time for hydrogen concentrations higher than 4000 ppm was within a few seconds, the recovery time became slow. This recovery behavior was similar to that for the Pt/Ga₂O₃/n-SiC structure device when biased in the reverse direction.

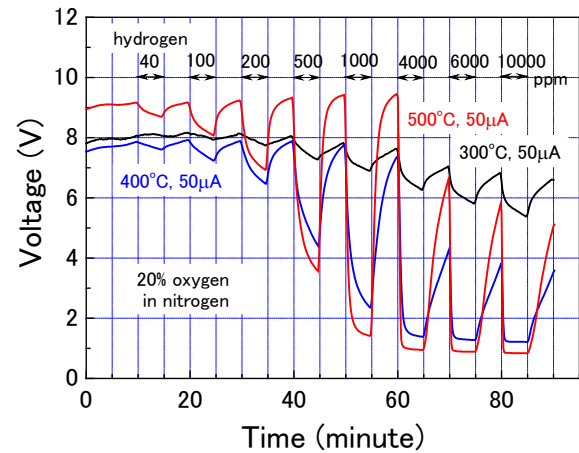


Figure 8. Response voltage curves for the Pt/Ga₂O₃/p-SiC gas sensor device with intermittent increases in the H₂ concentration in a 20% O₂ / N₂ atmosphere at 300, 400 and 500 °C. The forward bias current of the device was kept at 50 μA.

In the measurement of the response curve shown in Fig. 8, the temperature of the device rose and fell by around 1 °C for each temperature condition at intervals of about 10 min. These temperature fluctuations did not have a large influence on the response of the device.

Because the present sensor devices with Pt/Ga₂O₃/n-SiC or Pt/Ga₂O₃/p-SiC structure are fabricated from semiconductor materials, the sensor devices must be influenced by temperature fluctuation. If the sensors are used under the condition with large temperature fluctuation, the temperature compensation system should be contrived as we demonstrated in the previous report (Nakagomi et al., 2013a).

3.2.3 Comparison between Pt/Ga₂O₃/n-type SiC and Pt/Ga₂O₃/p-type SiC devices

Figure 9 shows the relationship between the sensor voltage output under a constant current of 50 μA and various hydrogen concentrations at 300, 400 and 500 °C. Figure 9 was constructed from the response curves shown in Figs. 7 and 8. Both the Pt/Ga₂O₃/n-type SiC device biased in reverse and the Pt/Ga₂O₃/p-type SiC device biased forward are included in Fig. 9. When the hydrogen concentration was increased in 20% O₂ / N₂ at 300 °C, there was a baseline drift for both devices. However, the output voltage decreased largely in the region between 200 and 1000 ppm hydrogen at 400 and 500 °C. The change in output voltage is caused by the reaction between oxygen and hydrogen, which was noted in one of our previous works (Nakagomi et al., 2011a). For example, the voltage output decreases significantly for 200 ppm hydrogen in 20% O₂ / N₂. Therefore, the present sensor device could detect hydrogen concentrations lower than 1/200 of the explosion limit of hydrogen gas in air. Thus the concentration ratio of H₂ / O₂ is 1/1000.

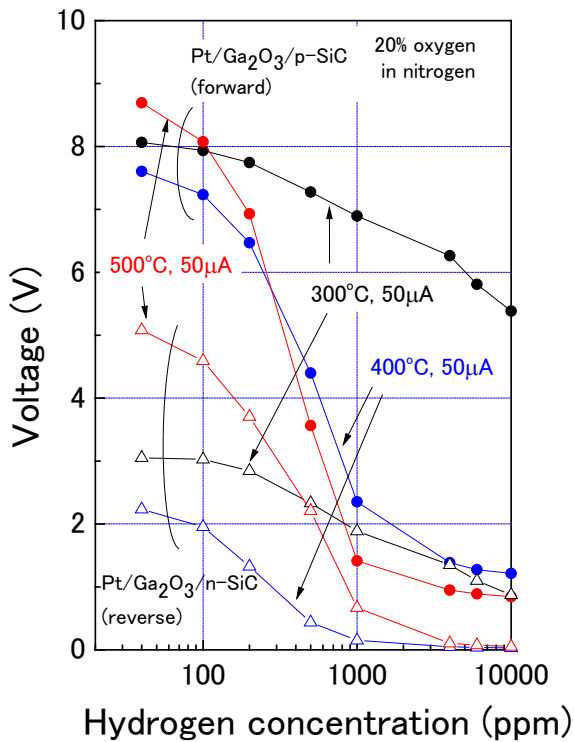


Figure 9. Relationship between the voltage response and hydrogen concentration for the Pt/Ga₂O₃/n-SiC and Pt/Ga₂O₃/p-SiC devices in a 20% O₂ / N₂ atmosphere at 300, 400 and 500 °C.

4 Discussion

4.1 Energy band diagram

The expected band diagram for the hydrogen gas sensor device based on the Pt/Ga₂O₃/n-SiC and Pt/Ga₂O₃/p-SiC structures under zero bias is shown in Fig. 10a and b. β-Ga₂O₃ has a wider band gap than 6H-SiC, and the electron affinity of β-Ga₂O₃ and 6H-SiC has been reported as 4.0 and 3.45 eV, respectively (Mohamed et al., 2012; Davydov 2007). Therefore, the offset in the conduction band, ΔE_C of 0.55 eV, and the offset in the valence band, ΔE_V of 2.43 eV, should exist at the heterointerface in the ideal case. As a result, it is estimated that there was a barrier ($qV_D - \Delta E_C$) of 0.45 eV for conduction electrons in n-type SiC of the Pt/Ga₂O₃/n-SiC structure. V_D is the sum of the built-in potential formed at both sides of heterointerface. For the Pt/Ga₂O₃/p-SiC structure device, the barrier ($qV_D + \Delta E_C$) for conduction electrons in the Ga₂O₃ layer is 2.28 eV. A Schottky barrier of 1.65 eV is also formed between Pt and the β-Ga₂O₃ layer if the work function of Pt is 5.65 eV. However, it is known that this Schottky barrier height is changed depending on the hydrogen concentration in the atmosphere.

It is important that holes in the SiC region not be able to flow into the β-Ga₂O₃ layer, because the energy barrier of 4.16 eV for holes from p-type 6H-SiC to β-Ga₂O₃ is

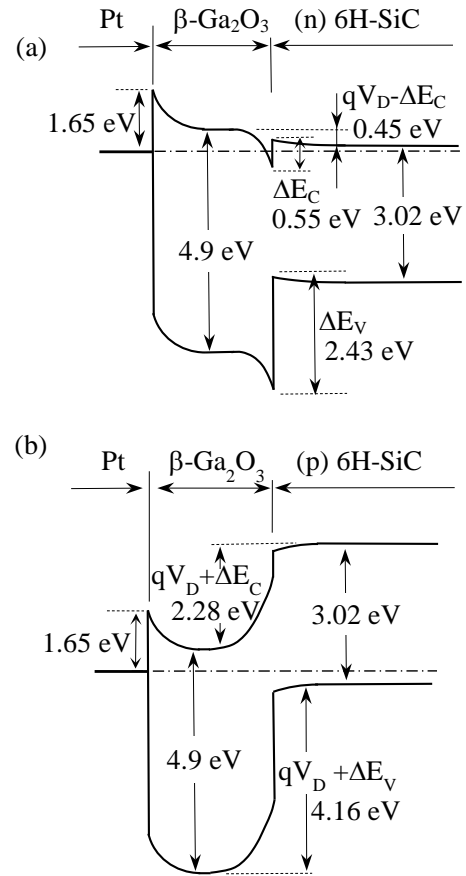


Figure 10. Energy band diagrams for hydrogen gas sensor devices based on the (a) Pt/Ga₂O₃/n-SiC and (b) Pt/Ga₂O₃/p-SiC structures.

considerably higher than the barrier of 2.28 eV for conduction electrons from β-Ga₂O₃ to p-type 6H-SiC when p-type SiC is used as a substrate. Even when n-type SiC is used as substrate, the energy barrier for holes from n-type 6H-SiC to β-Ga₂O₃ of 2.43 eV is considerably higher than the barrier for conduction electrons from 6H-SiC to β-Ga₂O₃ in the conduction band. Therefore, only electrons can be considered as the charge carriers for both device structures.

4.2 Ga₂O₃/n-type SiC heterojunction device

We considered reasons why the device based on heterojunctions of Ga₂O₃/n-type SiC has hydrogen-sensing properties for each bias condition. Figure 11a and b show schematic band diagrams for the Pt/Ga₂O₃/n-type SiC structure in the forward and reverse bias directions, respectively. The applied voltage of the device V is distributed to the bias voltage V_1 applied to the Schottky junction and the bias voltage V_2 applied to the n-n heterojunction between Ga₂O₃ and n-type SiC.

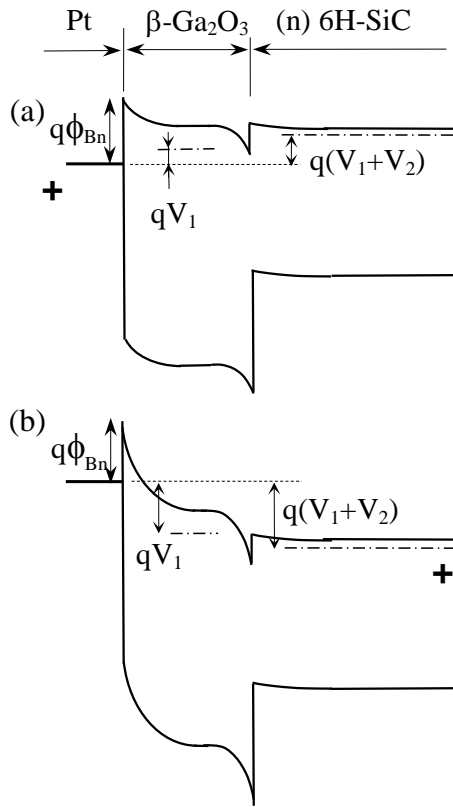


Figure 11. Energy band diagrams for a hydrogen gas sensor device based on the Pt/Ga₂O₃/n-SiC structure biased in the (a) forward and (b) reverse directions.

The current of the Schottky diode is given by

$$I_1 = SA^*T^2 e^{-\frac{q\phi_{Bn}}{kT}} \left(e^{\frac{qV_1}{kT}} - 1 \right), \quad (1)$$

where S is area of the device, A^* is the effective Richardson's constant, T is absolute temperature, q is the charge of an electron, and $q\phi_{Bn}$ is the Schottky barrier height (Sze and Ng, 2007).

Only electron flow can be considered in the Pt/Ga₂O₃/n-type SiC structure device; therefore, the current of the n-n heterojunction between Ga₂O₃ and n-type SiC is given by

$$I_2 = SB e^{-\frac{qV_D - \Delta E_C}{kT}} \left(e^{\frac{qV_2}{kT}} - 1 \right), \quad (2)$$

where S is the area of the device, B is constant including several parameters, ΔE_C is the offset in the conduction band between β -Ga₂O₃ and 6H-SiC, and V_D is the sum of the built-in potential formed at both sides of the heterointerface, i.e., $(qV_D - \Delta E_C)$ is the barrier height for electrons to migrate from n-type 6H-SiC to β -Ga₂O₃ (see Fig. 10a). In addition, the Schottky diode and heterojunction of Ga₂O₃/n-type SiC are connected in series; therefore

$$I_1 = I_2. \quad (3)$$

When the device with the Pt/Ga₂O₃/n-type SiC structure is forward biased, both the Schottky junction and the n-n heterojunction are biased in the forward direction. Therefore, both V_1 and V_2 are positive. The band diagram in Fig. 11a shows that electrons in n-type SiC flow into the Ga₂O₃ region by getting over the barrier at the interface and flow to the Pt electrode over the Schottky barrier. In this case, two barriers are lowered because both barriers are forward biased. When the barrier $q\phi_{Bn}$ is lowered due to hydrogen gas exposure, the flow of electrons from Ga₂O₃ to Pt is increased. However, the influence of the barrier height change is small because the Schottky junction is already biased in the forward direction and the barrier height for conduction electrons from Ga₂O₃ to Pt is already lowered.

The barrier for electron transport from Ga₂O₃ to Pt is higher than the barrier of $qV_D - \Delta E_C$ from n-type SiC to Ga₂O₃; therefore, $V_1 \gg V_2$ and assume $V = V_1$, and so

$$V = \phi_{Bn} + \text{const.} \quad (4)$$

This equation indicates that a change in ϕ_{Bn} is equivalent to a change in applied voltage, V . Therefore, when the ϕ_{Bn} is changed depending on the hydrogen concentration in the atmosphere, the variation appears directly in the applied voltage.

The hydrogen sensor with the Pt/Ga₂O₃/n-type SiC structure reported by Trinchi et al. (2004) was used under forward bias conditions (Trinchi et al., 2004). The sensor device corresponds to the same situation; therefore, the present results indicate similar I - V characteristics to those reported by Trinchi et al. (2004).

When the Pt/Ga₂O₃/n-type SiC structure device is biased in reverse, both the Schottky junction and the n-n heterojunction are biased in the reverse direction. However, because $q\phi_{Bn} \gg \Delta E_C$, almost all of the voltage is applied to the Schottky junction. Thus, the ΔE_C barrier does not act as an obstacle. Almost all of the electron flow is determined by electrons that can get over the barrier from the Pt electrode to β -Ga₂O₃ layer; therefore, the current is mainly determined by the Schottky barrier height, $q\phi_{Bn}$. A change in ϕ_{Bn} thus leads to a change in the I - V characteristics. This situation corresponds to the case of a single Schottky diode. Therefore, the current is given by

$$I = -SA^*T^2 e^{-\frac{q\phi_{Bn}}{kT}}. \quad (5)$$

4.3 Ga₂O₃/p-type SiC heterojunction device

Figure 12a and b show schematic band diagrams for the Pt/Ga₂O₃/p-type SiC structure biased in the forward and reverse directions, respectively. V_1 and V_3 correspond to the bias voltage applied to the Schottky junction and to the n-p heterojunction between β -Ga₂O₃ and p-type SiC, respectively.

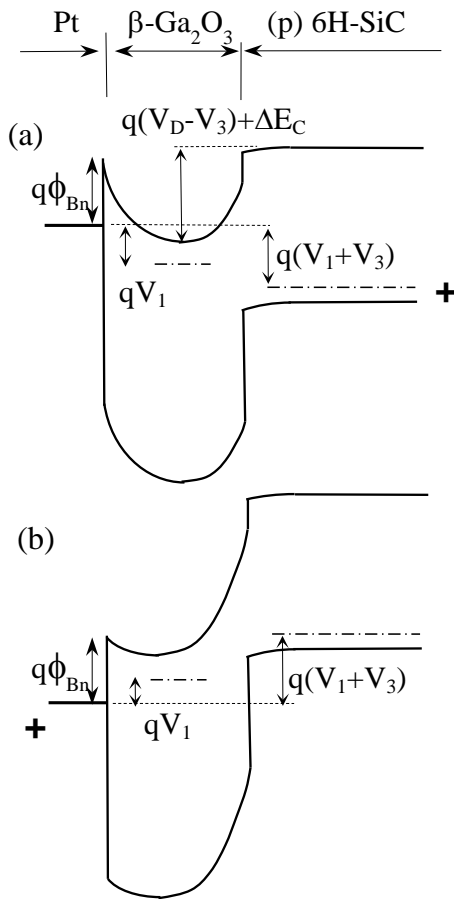


Figure 12. Energy band diagram for a hydrogen gas sensor device based on the Pt/Ga₂O₃/p-SiC structure biased in the (a) forward and (b) reverse directions.

Only the electrons are considered as charge carriers; therefore, the current of the n–p heterojunction is given by

$$I_3 = SB e^{-\frac{qV_D + \Delta E_C}{kT}} \left(e^{\frac{qV_3}{kT}} - 1 \right). \quad (6)$$

When the device is biased in the forward direction, the Schottky junction between the Pt electrode and the β -Ga₂O₃ layer is biased in the reverse direction, while the n–p heterojunction is biased in the forward direction. The electrons in the β -Ga₂O₃ region flow to the p-type SiC region over the potential barrier in the conduction band. The barrier is lowered with increasing forward bias; however, the Schottky junction is biased in reverse; therefore, only those electrons that can get over the Schottky barrier flow into the β -Ga₂O₃ region and can also reach the SiC region. When $q\phi_{Bn}$ is lowered due to hydrogen gas exposure, the electrons are increased and the current is thus increased. This increase in electrons getting over the Schottky barrier corresponds to a decrease in electrical resistance.

This process allows us to expect a saturation property in I – V characteristics observed in Fig. 6. Because the forward current does not quite increase with an increase in bias voltage due to electron flow limited by the Schottky barrier, the current is saturated. If the electron flow from the Schottky barrier is increased with an increase in hydrogen concentration, the saturation current level also rises.

The voltage applied to the device is shared by both the Schottky junction and heterojunction:

$$V_1 + V_3 = V. \quad (7)$$

Therefore, under constant applied voltage, the decrease in voltage shared at the Schottky junction V_1 due to a decrease in electrical resistance leads to an increase in the voltage shared at the heterojunction V_3 . Thus, the flow of electrons is increased by this amplification effect. This is the mechanism under the forward bias condition.

When the device is biased in the forward direction, $e^{\frac{qV_1}{kT}}$ in Eq. (1) and 1 in Eq. (6) are omitted.

Using $-I_1 = I_3$,

$$(qV_D + \Delta E_C) - qV_3 = q\phi_{Bn} - \text{const.} \quad (8)$$

When ϕ_{Bn} is decreased, V_3 must be increased, which leads to a lowering of the $q(V_D - V_3) + \Delta E_C$ barrier height and the increase in electron flow increases the forward current exponentially. We consider that this amplification effect leads to the large change in the forward current.

In contrast, when the device is biased in the reverse direction, 1 in Eq. (1) and $e^{\frac{qV_3}{kT}}$ in Eq. (6) are omitted to give

$$q(\phi_{Bn} - V_1) = \Delta E_C + qV_D + \text{const.} \quad (9)$$

Therefore, if ϕ_{Bn} is decreased, V_1 will also be decreased. However, almost all of the applied voltage is applied to the reverse bias of the n–p heterojunction between Ga₂O₃ and p-type SiC, and because the Schottky junction is already biased in forward direction, the device has low hydrogen sensitivity.

5 Conclusions

Field-effect hydrogen gas sensor devices based on Pt/Ga₂O₃/SiC heterojunction structures were fabricated. Two types of hydrogen gas sensor devices were fabricated with Pt/Ga₂O₃/n-type SiC heterojunction and Pt/Ga₂O₃/p-type SiC heterojunction structures. The I – V characteristics were measured and the hydrogen response properties were evaluated with respect to the bias conditions. Both the sensor with the Pt/Ga₂O₃/n-type SiC structure biased in reverse and that with the Pt/Ga₂O₃/p-type SiC structure forward biased had large responses; when the Schottky junction between Pt and β -Ga₂O₃ is biased in reverse, the sensors have a large response. The sensors could detect 40 ppm hydrogen for certain under 20% O₂/N₂ at 500 °C under appropriate bias conditions. The behavior of the hydrogen

sensing was explained using several band diagrams for bias in the forward and reverse directions.

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