

Hydrogen Gas Sensor Based on β -Ga₂O₃ Thin Film with a Function of Self Temperature Compensation

*Shinji Nakagomi, Tsubasa Sai, Yoshihiro Kokubun
Ishinomaki Senshu University, Ishinomaki Miyagi 986-8580 Japan,
nakagomi@isenshu-u.ac.jp*

Abstract:

Field effect Hydrogen gas sensor devices based on β -Ga₂O₃ thin films with a function of temperature compensation were fabricated. β -Ga₂O₃ thin films were deposited on sapphire substrate by gallium evaporation in oxygen plasma. Resistance between two ohmic electrodes on β -Ga₂O₃ thin film with Pt gate was decreased in H₂ ambient. The sensor can detect 100ppm H₂ under 20%O₂ at 400°C. The resistance of the device without gate little changes for an ambient variation. By connecting the devices with and without gate in series, the devices have a function of self temperature compensation. It was demonstrated that the device kept stable output even for temperature fluctuation over 100°C.

Key words: Gallium oxide, hydrogen, high temperature, Field effect, temperature compensation

Introduction

Many gas sensors based on Ga₂O₃ have been studied [1,2]. However, film sintered from powder or thin film of poly crystal prepared by sputtering has been used as sensing material. Ga₂O₃ acted as a gas-sensitive electrical resistance even in MOS structure using Ga₂O₃ layer and SiC reported by Trinchi et al [3]. Nakagomi et al. studied hydrogen sensor with Schottky diode structure based on Ga₂O₃ single crystal [4,5].

In case where the sensor is used under the high temperature condition, temperature fluctuation affects sensor output. Thus, Temperature compensation is effective under the unstable temperature condition [6]. In this paper, field effect hydrogen sensor based on Ga₂O₃ thin film is studied and proposed new method of temperature compensation.

Experimental

β -Ga₂O₃ thin films were prepared on (0001) sapphire substrate by gallium evaporation in oxygen plasma. The substrate temperature was set at 600°C. After oxygen gas of 4 sccm was flowed into the vacuum chamber and discharged by rf-power of 100W, gallium was evaporated and formed β -Ga₂O₃ thin films of which thickness is about 1 μ m.

In the beginning, transmission spectrum of the deposited Ga₂O₃ films was measured. Absorption coefficient was calculated from the spectrum and energy band-gap of the film was

estimated to 4.9 eV. This wide band-gap enables high temperature operation.

Figure 1 shows one example of X-ray diffraction patterns in $\theta-2\theta$ scan of the films. The diffraction peaks indexed to (-201) plane of β -Ga₂O₃ and a peaks of (0001) plane of sapphire were mainly observed. Then the β -Ga₂O₃ films are mainly oriented to (-201) plane though a smaller (010) peak of β -Ga₂O₃ was also observed.

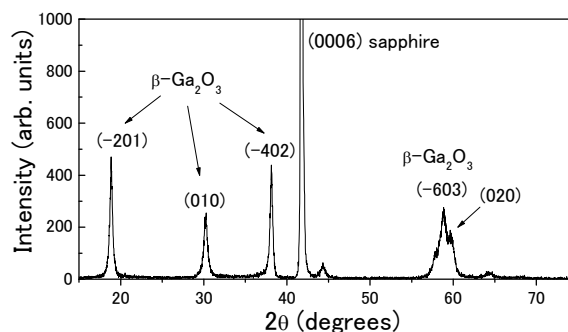


Fig. 1 X-ray diffraction patterns of β -Ga₂O₃ thin film prepared on (0001) sapphire substrate.

Schematic drawing of the device structure is shown in Fig. 2 (a). Ohmic (source and drain) electrodes of Ti/Al/Pt/Au and Pt gate electrode were prepared on the Ga₂O₃ thin film by a lift-off process and annealing. Two types device were fabricated on the same wafer. One is a resistance device with two ohmic electrodes and the other is a sensor device with two ohmic electrodes and Pt gate electrode.

Figure 2 (b) shows a picture of the sensor device with electrodes of source, drain and gate. Distance between the source and drain electrode is about 450 μm . The devices were set in a quartz cube in a furnace. Current-voltage (I-V) characteristics for each devices were measured in 20%O₂ in N₂ or 200ppm H₂ in N₂ atmospheres at 200~500°C. When the electrical properties between the source and drain electrode were measured, Pt gate electrode of the sensor is floating. Voltage response curves were also measured under constant current condition for the sensor devices.

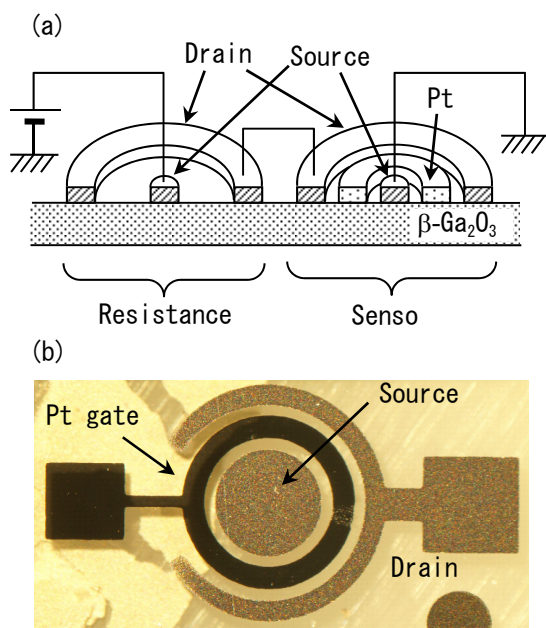


Fig. 2 (a) Structure of the hydrogen gas sensor device based on $\beta\text{-Ga}_2\text{O}_3$ thin film. Resistance device has no gate and sensor device has Pt gate electrode. Two devices were connected in series for self temperature compensation. (b) Picture of the sensor device with gate electrode.

Principle of Field Effect Sensor Device

Current between two ohmic electrodes (source and drain electrodes) flows through Ga_2O_3 layer. Pt formed as gate builds Schottky barrier at the surface of Ga_2O_3 . Barrier height of the Schottky varies depending on the ambient of the device. Depletion layer of the barrier affects effective width for current flow and leads to a change in electrical resistance. Thus, device with gate becomes gas sensor. Principle of this field effect gas sensor device is same as our previous work based on GaN [7]. According to this principle, devices without gate don't have a function of gas sensor.

Hydrogen Sensing Properties

Current-voltage (I-V) characteristics of the sensor devices without and with gate electrode were measured at 400°C. I-V characteristics of two type's devices without and with gate electrode were almost linear in 20%O₂ ambient and in 200ppm H₂ ambient. I-V characteristics of the device without gate were little influenced by ambient gas. In contrast, I-V characteristics of the device with gate were changed for a change in ambient as shown in Fig. 3. This suggests that gate electrode leads to a sensing behavior.

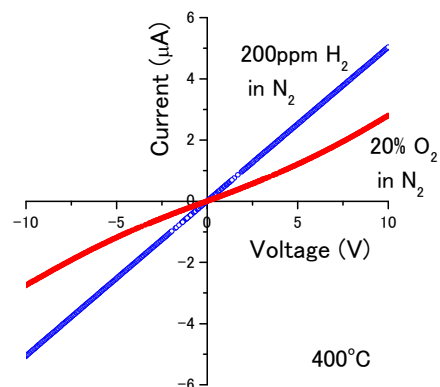


Fig. 3 Current-voltage characteristics of the gas sensor device based on $\beta\text{-Ga}_2\text{O}_3$ thin film with Pt gate electrode in 20% O₂ in N₂ and 200ppm H₂ in N₂ atmospheres at 400°C.

Fig. 4 shows voltage response curves in the device with gate under constant current (2 μA) for an intermittent increase in H₂ concentration under 20% O₂ in N₂ at 400°C. The voltage changed with an increase in H₂ concentration. And the voltage changed sharply at the region of 500-1000ppm H₂.

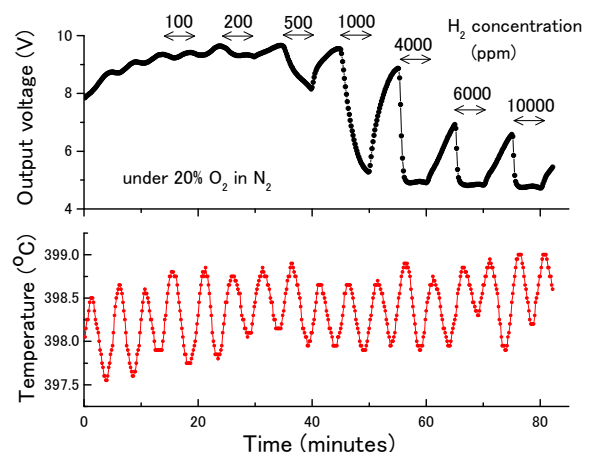


Fig. 4 Response curves of the voltage of the gas sensor device with Pt gate electrode for an intermittent increase in H₂ concentration under 20% O₂ in N₂ at 400°C.

It was demonstrated that the sensor device can detect hydrogen gas in air. However, the temperature fluctuated a little during measurement as shown in Fig. 4. It was caused by a control of the furnace. Fluctuation of just 1°C gave rise to the fluctuation of output voltage. Because Ga_2O_3 is a semiconductor, electrical resistances in the device is decreased with an increase in temperature. Therefore, temperature fluctuation makes difficult to sense lower concentration gas.

Temperature Compensation

We propose temperature compensation based on series connection of two devices without and with gate electrode. As shown in Fig. 5, two resistances connected in series and dc voltage is supplied.

Assuming two resistances are given by

$$R_A = R_{A0} e^{\frac{\alpha}{T}} \quad (1)$$

$$\text{and } R_B = R_{B0} e^{\frac{\beta}{T}} \quad (2)$$

where α and β are temperature coefficient, output voltage V_{out} is given as

$$V_{out} = \frac{V_0}{\frac{R_A}{R_B} + 1} = \frac{V_0}{\frac{R_{A0}}{R_{B0}} e^{\frac{\alpha-\beta}{T}} + 1} \quad (3)$$

If α is equal to β , V_{out} is not influenced by temperature. The values of α and β may be nearly same because the two devices without and with gate are fabricated using same Ga_2O_3 layer on wafer. This means that the connected sensor is stable for a temperature fluctuation.

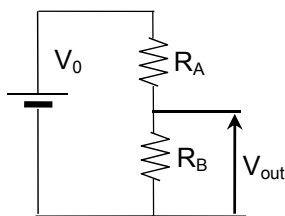


Fig. 5 Circuit for measurement of the series connection of two devices with and without gate.

Fig. 6 shows both the output voltage of a single sensor device under constant current (2 μA) and the output voltage of two devices connection under constant ambient of 1000ppm H_2 and 20% O_2 in N_2 . 10 volts were applied to the series connection of two devices with and without gate

shown in Fig. 2, and voltage between the source and drain electrode of the device with gate was measured as output voltage. Variation of temperature is also shown in Fig. 6.

When the temperature was perturbed over 20°C intentionally, the output voltage of single sensor device varied depending on a change in temperature. In contrast, the output voltage of the series connection of two devices with and without gate was kept stable.

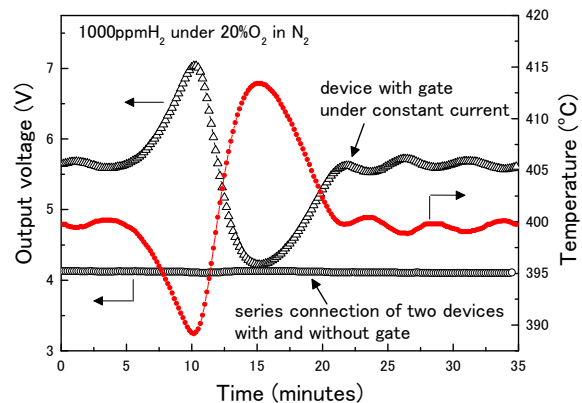


Fig. 6 Fluctuation of output voltage of the single sensor device and of the series connection of two devices with and without gate when the temperature was disturbed deliberately.

Fig. 7 (a) and (b) shows output voltage of the single sensor device and of the series connection of two devices with and without gate, respectively. 0.4% H_2 was injected intermittently into constant 20% O_2 ambient with 3 minutes interval. Variation of temperature is also shown in Fig. 7 (a) and (b).

Constant current of 5 μA was supplied to the single sensor device with gate, and voltage between the source and drain electrode was measured as output signal. The output voltage responded to variation of ambient gas in condition of constant temperature as shown in Fig. 7 (a). When the temperature was decreased suddenly from 500°C to 450°C on purpose and was returned, the output voltage of single sensor device was increased with lowering temperature and decreased with increasing temperature because of temperature dependence of electric resistance of $\beta\text{-Ga}_2\text{O}_3$ film. Therefore, it is not possible to use the single sensor device in situation of large temperature fluctuation.

Fig. 7 (b) shows a case of series connection of two devices with and without gate. 10 volts were applied and voltage between the source and drain electrode of the device with gate was measured. Variation of ambient gas is same as the case of single device shown in Fig. 7 (a).

The temperature was decreased largely from 500°C to 400°C and returned. The output voltage was little affected even by large temperature fluctuation over 130°C. This demonstrates that the series connection of two devices with and without gate acts as hydrogen sensor with a function of temperature compensation. This series connection of the devices with and without gate is useful for gas detection in condition with large temperature fluctuation.

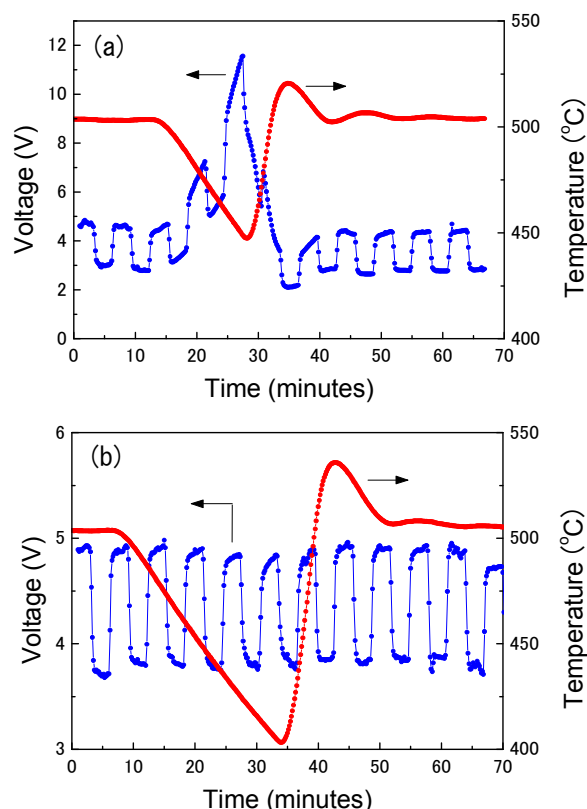


Fig. 7 Fluctuation of output voltage of the single sensor device (a) and of the series connection of two devices with and without gate (b) when the temperature was disturbed on purpose. 0.4% H₂ was injected intermittently into constant 20% O₂ ambient with 3 minutes interval.

In addition, it is also necessary to pay attention to dependence of electrical resistance of Ga₂O₃ itself on ambient gas under temperature condition higher than nearly 600°C. At the time, electrical resistance of the device without gate seems to be changed by ambient. Thus the series connection cannot cancel the temperature fluctuation effectively.

Conclusions

Field effect hydrogen gas sensor devices based on β-Ga₂O₃ thin films with a function of

temperature compensation were fabricated. Resistance between two ohmic electrodes without gate little changes for an ambient variation. Resistance between two ohmic electrodes with Pt gate was decreased in H₂ ambient. The sensor can detect 100ppm H₂ under 20%O₂ at 400°C. By connecting the devices with and without gate in series, the devices have a function of self temperature compensation. It was demonstrated that the device kept stable output even for temperature fluctuation over 100°C.

References

- [1] M. Fleischer, H. Meixner, Sensing reducing gases at high temperatures using long-term stable Ga₂O₃ thin films, *Sens. & Actuators B*, 6, 1/3, 257-261 (1992); doi:10.1016/0925-4005(92)80065-6
- [2] M. Fleischer, J. Giber, H. Meixner, H₂-Induced Changes in Electrical Conductance of β-Ga₂O₃ Thin-Film Systems, *Appl. Phys.*, A54, 560-566 (1992); doi:10.1007/BF00324340
- [3] A. Trinchì, W. Włodarski, Y. X. Li, Hydrogen sensitive Ga₂O₃ Schottky diode sensor based on SiC, *Sens. & Actuators B*, 100, 1/2, 94-98 (2004); doi:10.1016/j.snb.2003.12.028
- [4] S. Nakagomi, M. Kaneko, Y. Kokubun, Hydrogen Sensitive Schottky Diode Based on β-Ga₂O₃ Single Crystal, *Sensor Letters*, 9, 1, 35-39 (2011); doi:10.1166/sl.2011.1413
- [5] S. Nakagomi, M. Ikeda, Y. Kokubun, Comparison of Hydrogen Sensing Properties of Schottky Diodes Based on SiC and β-Ga₂O₃ Single Crystal, *Sensor Letters*, 9, 2, 616-620 (2011); doi:10.1166/sl.2011.1575
- [6] K. Tsukada, M. Kariya, T. Yamaguchi, T. Kiwa, H. Yamada, T. Maehara¹, T. Yamamoto, S. Kunitsugu, Dual-Gate Field-Effect Transistor Hydrogen Gas Sensor with Thermal Compensation, *Jpn. J. Appl. Phys.*, 49, 024206 (2010); doi:10.1143/JJAP.49.024206
- [7] T. Higuchi, S. Nakagomi, Y. Kokubun, Field Effect Hydrogen Sensor Device with Simple Structure Based on GaN, *Sens. & Actuators B*, 140, 79-85 (2009); doi:10.1016/j.snb.2009.04.031