



Title	A study on hydrogen adsorption of Metal-Insulator-Silicon sensor with La₂O₃ as gate insulator
Author(s)	Chen, G; Lai, PT; Yu, J
Citation	The 2010 IEEE International Conference of Electron Devices and Solid-State Circuits (EDSSC 2010), Hong Kong, China, 15-17 December 2010. In IEEE EDSSC Proceedings, 2010, p. 1-4
Issued Date	2010
URL	http://hdl.handle.net/10722/160264
Rights	IEEE Conference on Electron Devices and Solid-State Circuits Proceedings. Copyright © IEEE.

A Study on Hydrogen Adsorption of Metal-Insulator-Silicon Sensor with La_2O_3 as Gate Insulator

Gang Chen¹, P.T. Lai¹, Jerry Yu²

¹Dept. of Electrical & Electronic Engineering
The University of Hong Kong
Hong Kong, P.R. China
Email: laip@eee.hku.hk

²School of Electrical & Computer Engineering
RMIT University
Melbourne, Australia

Abstract – A new Metal-Insulator-Silicon (MIS) Schottky-diode hydrogen sensor with La_2O_3 as gate insulator was fabricated. Its hydrogen-sensing properties were studied from room temperature (RT) to 200°C. Results showed that the device had excellent hydrogen-sensing performance below about 250°C. Furthermore, hydrogen reaction kinetics was confirmed for the sample. The response time extracted from its hydrogen adsorption transient behavior was around 4.5 s at 150°C, while a hydrogen adsorption activation energy of 10.9 kcal/mol was obtained for the sensor.

Keywords – silicon; Schottky diode; hydrogen sensor

hydrogen adsorption characteristics of a Metal-Insulator-Silicon (MIS) Schottky-diode hydrogen sensor with La_2O_3 as gate insulator.

II. EXPERIMENT

Hydrogen sensor with the structure shown in Fig. 1 was fabricated. The n-type Si (100) substrate (0.5 ~ 0.7 Ωcm) was cleaned in acetone in a pyrex glass beaker for 5 min. This was followed by rinsing in isopropanol for 2 min and DI water. The native oxide layer on the Si substrate was removed by dipping in 5% hydrofluoric acid for 10 sec. Subsequently, the Si substrate was rinsed in DI water and blown dry with nitrogen gas.

A 40-nm Ti layer and a 100-nm Pt layer were then deposited in sequence on the back of the Si substrate by DC sputtering of Ti and Pt, respectively to form an ohmic contact. A second cleaning process followed. Since the deposition caused a growth of a thin native oxide layer on the surface of the Si substrate, the native oxide layer was removed with a dipping in 5% hydrofluoric acid for 10 sec. The Si substrate was then cleaned in DI water and blown dry with nitrogen gas.

The gate insulator, a 4-nm La_2O_3 layer, was deposited at room temperature by RF sputtering of La_2O_3 in a mixed Ar/ O_2 ambient (Ar to O_2 ratio = 4:1). The front electrode, a 100-nm Pt layer with a diameter of 0.5 mm, was then deposited on the gate insulator by DC sputtering of Pt through a stainless-steel shadow mask. Finally, the sample underwent an annealing in a furnace at 500°C in nitrogen gas (1000 ml/min) for 30 min.

I. INTRODUCTION

Recently, instead of petroleum, hydrogen gas has been considered as a clean energy source [1]. For safety reasons, the determination of hazardous hydrogen concentration in air (4.65 ~ 74.5%) is an important issue in many areas of human activity [2].

From the hydrogen detection point of view, high-sensitivity hydrogen sensor based on Schottky diode with catalytic Pt metal can be a suitable candidate because the Schottky-diode current depends exponentially on the change of Schottky barrier height. In addition, Schottky diodes with a thin oxide layer exhibit higher sensitivity and larger modulation of barrier height. It has been pointed out that small barrier height and high leakage current resulted from high surface-state density could be improved by the use of an interfacial oxide layer [3].

Lanthanum oxide (La_2O_3) thin films have a large range of applications in electronics, optics and catalysis. Due to its high relative permittivity ($k \sim 27$), large band gap (6 eV) and thermal stability when deposited on silicon substrate, lanthanum oxide is a promising gate oxide material for future applications [4]. Therefore, the objective of this work is to investigate the

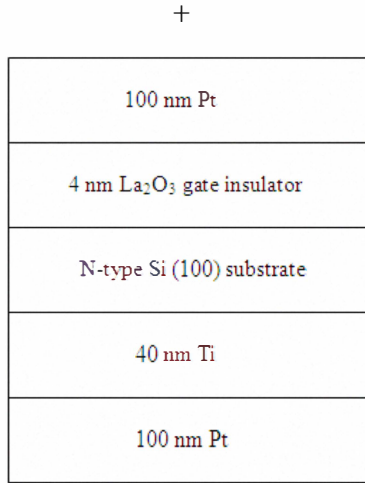


Fig. 1 Structure of the hydrogen sensor

After fabrication of the hydrogen sensor, its hydrogen-sensing properties were studied. Measurements were carried out using a computer-controlled measurement system described in Fig. 2. A thermostat, a semiconductor parameter analyzer (HP4145B) and two digital gas flow controllers (DGFC) were connected to a computer and controlled by software programs. The test sample was placed in a stainless-steel closed chamber inside the thermostat, and gases were injected into the chamber through the digital gas flow controllers.

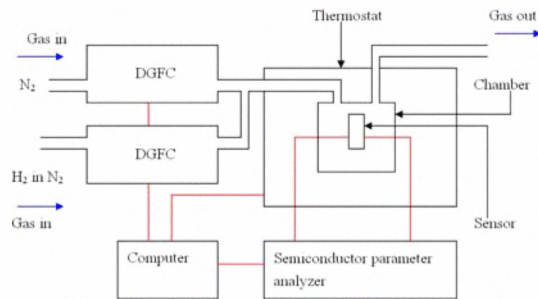


Fig. 2 Computer-controlled measurement system

III. RESULTS AND DISCUSSION

Fig. 3 depicts the sensitivity-temperature characteristics of the sensor. The sensitivity is defined as $(I_{H_2} - I_{air})/I_{air}$, where I_{H_2} and I_{air} are currents measured in hydrogen environment and air respectively. The sensitivity of the device initially increases and achieves its maximum value of 7.2 at 150°C, but then decreases as the temperature further increases. This phenomenon can be explained as follows [5-7]. When temperature increases (RT ~ 150°C), hydrogen molecules under higher pressure bombard the surface of the gate electrode more frequently.

Hence, more hydrogen molecules can adsorb at the surface of the electrode and also decompose faster into hydrogen atoms, giving higher sensitivity. On the other hand, the oxygen attached to the surface of the electrode (when the sensor is exposed to air) can react with the hydrogen atoms to form hydroxyl ions and water. The formation rates of these products increase rapidly at high temperature, thus decreasing the hydrogen atoms and the sensitivity. In addition, for even higher operating temperature (150°C ~ 200°C) (It is known that the operating temperature of the gas sensor using silicon substrate is limited to below about 250°C [8] primarily due to the small bandgap of silicon [9], and thus temperatures higher than 200°C were not considered), more electronic defects in the gate insulator are thermally activated and contribute to electrical conduction in the device. As a result, I_{air} increases more than I_{H_2} and thus the sensitivity decreases.

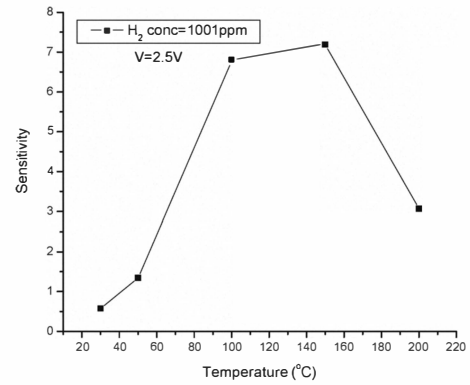


Fig. 3 Sensitivity vs. temperature characteristics of the sensor

Fig. 4 describes I_{air} and $\Delta I (= I_{H_2} - I_{air})$ as a function of temperature. In general, I_{air} increases with temperature due to thermionic emission, because at higher temperatures, more electrons have sufficient energy to overcome the potential barrier and flow through the Schottky diode.

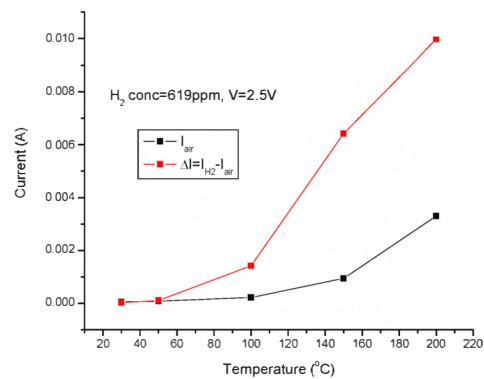


Fig. 4 I_{air} and ΔI of the sensor as a function of temperature

The Schottky barrier height (Φ_b) can be calculated as

$$\Phi_b = (K_B T/q) \ln(AA^{**} T^2 / I_0) \quad (1)$$

where K_B is the Boltzmann constant; T is the absolute temperature; A is the Schottky contact area; A^{**} is the effective Richardson constant; and I_0 is the saturation current.

Under steady-state condition, hydrogen coverage (θ) at the interface according to reaction kinetics can be represented as

$$\theta/(1-\theta) = k_0 (P_{H_2})^{0.5} \quad (2)$$

where k_0 is a constant and P_{H_2} is the hydrogen partial pressure. If the change in voltage across the hydrogen dipole layer (ΔV) induced by hydrogen adsorption is proportional to the hydrogen coverage, i.e., $\Delta V = \Delta V_{max} \theta$, then equation (2) can be written as

$$(\Delta V)^{-1} - (\Delta V_{max})^{-1} = (\Delta V_{max})^{-1} (k_0)^{-1} (P_{H_2})^{-0.5} \quad (3)$$

where ΔV_{max} is the maximum voltage change at a fixed temperature. After some calculation using equation (3) and equation (1), we obtain

$$\left[\ln(I_{0g}/I_0) \right]^{-1} = \left[\ln(I_{0gmax}/I_0) \right]^{-1} \left[1 + \frac{1}{(k_0)^{-1} (P_{H_2})^{-0.5}} \right] \quad (4)$$

where I_0 and I_{0g} are the saturation current and maximum saturation current in hydrogen environment respectively. Thus, the plot of $[\ln(I_{0g}/I_0)]^{-1}$ versus $(P_{H_2})^{-0.5}$ should be linear, with the y-intercept equal to $[\ln(I_{0gmax}/I_0)]^{-1}$ and the slope equal to $[k_0 \ln(I_{0gmax}/I_0)]^{-1}$. It is shown from Fig. 5 that the plot of $[\ln(I_{0g}/I_0)]^{-1}$ versus $(P_{H_2})^{-0.5}$ for the sensor is indeed linear. Thus, the theory and experimental data via the I-V analysis method confirm the hydrogen reaction kinetics in the sample [5, 8].

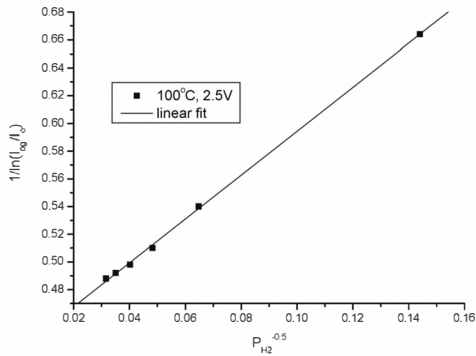


Fig. 5 Steady-state reaction kinetic analysis for hydrogen adsorption of the sensor at 100°C

The response time, which is defined at e^{-1} times the final steady-state value, can be obtained from the transient-response curve described in Fig. 6. As the temperature increases from RT to 50, 100, 150 and 200 °C, the response time of the sensor is 19.0, 11.7, 4.8, 4.5 and 8.4 s, respectively.

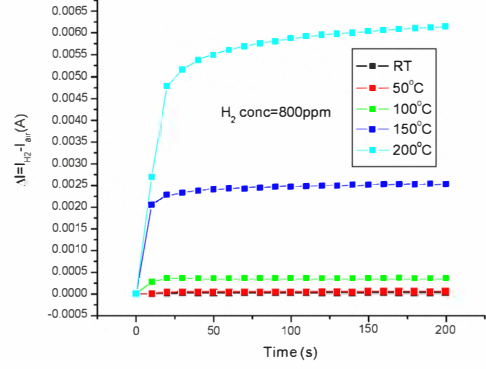


Fig. 6 Hydrogen adsorption transient behavior

As can be seen in Fig. 7, the hydrogen adsorption activation energy of the sensor can be derived by extracting the slope from the Arrhenius plot of current variation rate ($\Delta I/\Delta t$) versus the inverse of temperature ($1/T$). The activation energy is determined based on the highest current variation rate in the first 30 s (please refer to Fig. 6) upon exposure to 800-ppm H_2/N_2 for a temperature range from RT to 200 °C. The resulting Arrhenius plot yields an activation energy E_a of 10.9 kcal/mol ($E_a = -\text{slope} \times R \times 1000 = 5.51 \times 8.31 \times 1000 = 45.8 \text{ kJ/mol} = 10.9 \text{ kcal/mol}$) for the studied sensor. In others' work, the activation energy of a Pt/InN sensor is 7.60 kcal/mol, while that of a Pt/SiO₂/GaN is 2.89 kJ/mol [10].

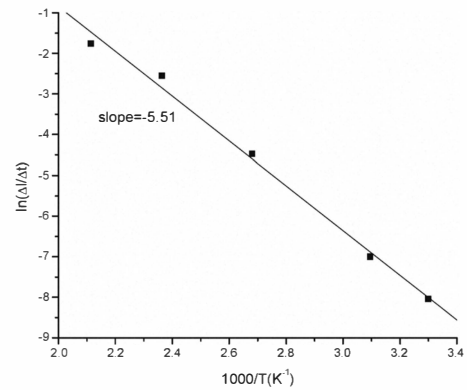


Fig. 7 Arrhenius plot of $\ln(\Delta I/\Delta t)$ vs. $1/T$

IV. CONCLUSIONS

Metal-Insulator-Silicon hydrogen sensor with La_2O_3 as gate insulator shows promising hydrogen-sensing properties below about 250°C , and the sensitivity can reach more than 7 at 150°C (H_2 conc. = 1001 ppm). We have confirmed the hydrogen reaction kinetics of the sample with I-V analysis. Moreover, the response time of the sensor is determined to be 4.5 s at 150°C , and the hydrogen adsorption activation energy is found to be 10.9 kcal/mol.

ACKNOWLEDGEMENT

This work is supported by the RGC of HKSAR, China (Project No. HKU 713510E), and the University Development Fund (Nanotechnology Research Institute, 00600009) of the University of Hong Kong.

REFERENCES

- [1] T.-H. Tsai, H.-I. Chen, K.-W. Lin, C.-W. Hung, T.-P. Chen, L.-Y. Chen, K.-Y. Chu, and W.-C. Liu, "A Pt/GaN Schottky Diode-Type Hydrogen Sensor with a Thin SiO_2 -Passivated Metal/Semiconductor Junction," 8th International Workshop on Junction Technology, pp. 164-167, 2008.
- [2] M. Ali, V. Cimalla, V. Lebedev, H. Romanus, V. Tilak, D. Merfeld, P. Sandvik, and O. Ambacher, "Pt/GaN Schottky diodes for hydrogen gas sensors," Sensors and Actuators B vol. 113, pp. 797-804, 2006.
- [3] Y.-Y. Tsai, S.-Y. Cheng, J.-H. Tsai, D.-F. Guo, H.-I. Chen and W.-C. Liu, "A new Pt-oxide-InAlP-based Schottky diode hydrogen sensor," International Solid-State Sensors Actuators and Microsystems Conference, pp. 2047-2050, 2007.
- [4] L. Ciontea, M. Nasui, T. Petrisor Jr., R.B. Mos, M.S. Gabor, R.A. Varga, and T. Petrisor, "Synthesis, crystal structure and thermal decomposition of $[\text{La}_2(\text{CH}_3\text{CH}_2\text{COO})_6(\text{H}_2\text{O})_3] \cdot 3.5\text{H}_2\text{O}$ precursor for high-k La_2O_3 thin films deposition," Materials Research Bulletin, vol. 45, pp. 1203-1208, 2010.
- [5] W.M. Tang, "MISiC Schottky-diode hydrogen sensors with different gate insulators," PhD thesis at The University of Hong Kong, 2008.
- [6] C.-C. Cheng, Y.-Y. Tsai, K.-W. Lin, H.-I. Chen and W.-C. Liu, "Hydrogen sensing properties of a Pt-oxide- $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$ high-electron-mobility transistor," Applied Physics Letters, vol. 86, pp. 112103, 2005.
- [7] X.F. Chen, W.G. Zhou, and O.K. Tan, "Microstructure, dielectric properties and hydrogen gas sensitivity of sputtered amorphous $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ thin films" Materials Science and Engineering B, vol. 77, pp. 177-184, 2000.
- [8] C.K. Kim, J.H. Lee, Y.H. Lee, N.I. Cho, and D.J. Kim, "A study on a platinum-silicon carbide Schottky diode as a hydrogen gas sensor," Sensors and Actuators B, vol. 66, pp. 116-118, 2000.
- [9] A. Trinchi, S. Kandasamy, and W. Wlodarski, "High temperature field effect hydrogen and hydrocarbon gas sensors based on SiC MOS devices," Sensors and Actuators B, vol. 133, pp. 705-716, 2008.
- [10] T.-H. Tsai, J.-R. Huang, K.-W. Lin, W.-C. Hsu, H.-I. Chen and W.-C. Liu, "Improved hydrogen sensing characteristics of a Pt/ SiO_2 /GaN Schottky diode," Sensors and Actuators B, vol. 129, pp.292-302, 2008