Effect of Annealed Si/Ti/Pt Hetero Structure on The Response Time and Signals of Hydrogen Sensors

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Abstract

Titanium (Ti) and platinum (Pt) films deposited on p-doped Si electrode were incorporated as gas sensitive electrodes in Kelvin and Floating Gate Field Effect Transistor (FG-FET) systems. The films were annealed in oxygen at 800°C. SEM and EDX characterization methods were employed to study the surface of these films. Work function changes with respect to various hydrogen concentrations have been measured as a function of temperature and humidity. The results show that nano grains of titanium silicide (TiSi₂) and Pt islands are formed after the annealing. Annealed TiSi₂/Pt films are well suitable to significantly stabilize FG-FET based hydrogen sensor. The sensors can detect H₂ in concentration range between 0.3% and 2% from room temperature up to 135°C. The response time is quite fast i.e. $t_{90} \sim 43.2$ seconds. An experiment on the stability has proved that signal pattern of the sensors remained stable one month after first conditioning.

Keywords: Hydrogen Sensor, Floating Gate Field Effect Transistor (FG-FET), Titanium Silicide (TiSi₂), Platinum

1. Introduction

Hydrogen (H₂) is predicted to be an alternative energy carrier in the future. It will be used in automotive industry and in local fuel cells. It can decrease the problem related to the green house warming by CO₂. On the other hand, hydrogen is dangerous due to its explosive character. Already a concentration of 4% can cause an explosion¹⁾.

Platinum is known as a chemical sensitive layer for hydrogen detection with the work function principle²⁾. Unfortunately, it has poor selectivity at room temperature³⁾ and will be unstable with increasing operating temperature above 60°C¹⁾. Huge efforts have been carried out to stabilize it by modifications. It has been reported also that the stability of FET based hydrogen sensor at high temperature can be improved with coating new material film of Pt/SnO₂ on the Pt surface³⁾. However, it should be noted that the response time decreases with increasing thickness of the SnO₂ film⁴⁾. To overcome the problem, in this work the SnO₂ film is not used and is replaced by annealing the film. Therefore, the sensitivity and stability of H₂ detection is enhanced at higher temperatures without decreasing the response time.

In this measurement concept, a Kelvin System and a Floating Gate Field Effect Transistor (FG-FET) are used as transducer to measure work function change $\Delta\Phi$ of gas sensitive films, and convert it into an electrical signal⁵⁾. An interesting advantage of this method is its sensitivity to physisorption as well as chemisorption, which are occurred at surface of the

film. Moreover, it can be operated at low temperature, which is an advantage to mobile systems⁶⁾.

2. Experimental

2.1 Preparation of the Ti/Pt films

FG-FET sensor system consists of a top electrode and FG-FET chip^{3,7)}. The electrodes have been made out of p-doped silicon. In order to detect hydrogen, 110.6 nm titanium (Ti) and 249.4 nm platinum (Pt) films were deposited by DC sputtering on the electrodes sequentially. The thickness of the layers is only limited by the dimension of the FG-FET sensor system and does not affect the performance. This is true due to the fact that sensing mechanism of the sensor is only on the surface of the film. Afterwards the electrodes were annealed using horizontal furnace (Carbolite) in oxygen flow of 600 cm³/min. In the annealing, the temperature was ramped up to 800°C at rate of 20°C/min, and then it was dwelled for 30 min. Finally, it was ramped down to ambient temperature at rate of 20°C/min. Cross section of the film after and before the annealing can be seen in Fig. 1. It can be observed that border between Si, Ti and Pt is very clear before the annealing, meanwhile the border can not be seen anymore after the annealing. It is predicted that the Si, Ti and Pt films were melted to build an alloy.

Figure 1. SEM image: Cross section of Ti/Pt film (a) before annealing and (b) after annealing.

2.2 Surface characterization

Surface morphology of the films was characterized by Scanning Electron Microscope (SEM). Before the annealing, surface of the film is dense¹⁾. After the annealing, nano grains of TiSi_2 and Pt islands are formed on the surface. The surface structure can be seen in Fig.2. This structure is expected to support spill over effect on the surface due to interaction between oxygen and hydrogen molecules. Pt and TiSi_2 will be a catalyst and a support material, respectively.

Figure 2. SEM image of the Ti/Pt surface after annealing in oxygen at 800°C.

Characterization of the films was also carried out using Energy-Dispersive X-Ray (EDX) to determine qualitative composition of the surface (see Fig. 3). In the resulting energy spectrum, Si and Ti can be observed besides Pt. This is a proof for forming TiSi_2 on the surface. Ti and Si do not react with the ambient oxygen because they are covered by Pt film. It is evident from the EDX pattern that O is significantly low in quantity after annealing.

Figure 3. EDX measurement of the Ti/Pt surface before and after annealing in oxygen at 800°C.

3. Work Function Change Measurement

3.1. Kelvin System

For the measurement in the Kelvin System (Besocke Delta Phi GmbH) related to the experimental FG-FET structure with gas sensitive film was driven the following attempt profile: After stabilization of the operating temperature of 100°C and 115°C, the measurement chambers are rinsed for 15 min with 100 ml/min synthetic air. Afterwards, H_2 gas with various concentrations is serially exposed to the film for total time of 2.25 hours. The gas is exposed for 15 min. The chambers are rinsed again with the synthetic air for 15 min. The result shows that the film reacts to H_2 concentrations as which can be seen in Fig. 4. The reversible and stable work function change $\Delta\Phi$ can be observed during measurement at the both temperatures. Work function change of the films decreases with increasing H_2 concentrations. Accordingly, the film will be applied as a H_2 sensitive film in the experimental FG-FET sensor system.

Figure 4. Work function change of the TiSi_2/Pt film to various H_2 concentrations in the Kelvin probe system at 100, 115°C and dry conditions.

3.2 FG-FET Sensor System

In the experimental FG-FET sensor system, the annealed electrode is mounted on a FG-FET chip to build a hydrogen sensor. In order to know ability of the sensor in hydrogen detection, several tests were carried out.

Temperature Effect on The TiSi_2/Pt Sensor

The temperature of the sensor is one of the most important parameters, because adsorption and desorption are temperature activated processes⁸⁾. Increasing the temperature improves the sensor's sensitivity to test gases. On the other hand, the temperature has an effect on the physical properties of the film which is used in the sensor. An experiment related to temperature effect on TiSi_2/Pt based the FG-FET sensor system was carried out. The sensor is exposed to 1% of H_2 for 15 minutes and rinsed with synthetic air for 15 minutes under dry condition. Operating temperature is varied from room temperature until 165°C . It can be seen from Fig. 5 that a significant temperature effect on the sensor is observed from room temperature until 135°C . The sensor signal drops if H_2 is present and returns closely to its initial state when H_2 disappears. It takes more than 15 minutes for the signal to achieve its stable state. However, a difference in the signal before and after the exposure of H_2 becomes noticeable when the temperature is increased. The difference is clearly visible when the temperature is above 135°C .

Figure 5. Temperature effect on the TiSi_2/Pt sensor under dry conditions.

Concentration Dependence of the TiSi_2/Pt Sensor

The response of the sensor to various hydrogen concentrations was investigated at the operating temperature of 95°C under dry conditions. In multiple steps the sensor is exposed to various hydrogen concentrations for 15 minutes with 15 minutes recovery time between each step. According to Fig. 6,

the sensor signal decreases with increasing H_2 concentrations. It can detect very well in H_2 concentration range between 0.3% and 2%. At higher concentrations above 0.7%, the signal quickly achieves a steady state. Compared to the Ti/Pt sensor, sensitivity and stability of the TiSi_2 sensor is better.

Figure 6. (a) Response of the TiSi_2/Pt sensor to various H_2 concentrations at 95°C under dry conditions (b) Response of the Ti/Pt sensor to various H_2 concentrations at 95°C under dry conditions.

Reproducibility of The TiSi_2/Pt Sensor

The reproducibility is one important criterion that determines the ability of the sensor. Regarding the stability of the sensor, an experiment was undertaken at which a sample was tested one month after the first exposure to hydrogen. Here the measurement conditions were room temperature and dry conditions. Fig. 7a proves that the sensor signals remain stable to 1% of H_2 gas exposure with response time $t_{90} \sim 43.2$ second. t_{90} is time, which is needed to reach 90% of maximum output signal as shown in Fig 7b. The reproducibility of the output signals is very well. No noticeable signal drifts can be observed after eight times of H_2 exposure cycles.

Figure 7. (a) Stability and reproducibility of the TiSi₂/Pt sensor toward 1% of H₂ exposure one month without testing after first conditioning at room temperature under dry conditions (b) Response time t_{90} .

Longterm Stability of The TiSi₂/Pt Sensor

Longterm stability of the sensor was investigated at 60°C under 30% relative humidity after six days without testing. The sensor is exposed to constant flow of dry synthetic air for 15 minutes with interrupted 0.5%, 1% and 2% of H₂ for 15 minutes. Afterwards it is rinsed with synthetic air for 24 hours. This cycle is repeated. Fig. 8 shows the long-term stability of the sensor. The signal pattern and the base line of the sensor still remain stable in the beginning of the measurement after six days without testing. The signals need more than 15 minutes to achieve real base line of the sensor.

Figure 8. Longterm stability of the TiSi₂/Pt sensor to H₂ at 60°C under 30% relative humidity after six days without testing.

Humidity Effect on The TiSi₂/Pt Sensor

From Fig. 9, it can be seen that $\Delta\Phi$ decreases with increasing relative humidity at each 0.9% H₂ concentration. In humid condition, water vapour will cover up the TiSi₂ surface, so function of TiSi₂ as the support material is not working. As consequently, only few oxygen species is absorbed at the TiSi₂ surface. The water vapour will draw H⁺ and O⁻ ions to form synthetic water at the TiSi₂ surface. However, it should be noted that hydrogen detection with the sensor is still possible.

Figure 9. Humidity effect of the TiSi₂/Pt sensor at room temperature.

3.3 Model of Gas Sensing Mechanism

The gas sensing mechanism is based on the spill-over effect due to the presence of dispersed metallic catalyst. If the sensors are exposed to synthetic air (20% O₂ and 80% N₂), the Pt catalyst dissociates directly O₂ molecule into O⁻ atom species. These species spill over onto TiSi₂. This causes a broadening of depletion layer at the conduction band near the surface of TiSi₂. As a result, the work function of TiSi₂ increases. Pt catalyst also dissociates directly H₂ molecule into H⁺ atoms, when the sensors are exposed to a mixture from H₂ and synthetic air. These atoms spill over onto TiSi₂ and react there with the O⁻ atom species. Adsorbed hydrogen atoms act as donors, which provide additional free electrons and induce an electron accumulation layer. As a result work function of TiSi₂ decreases leading to a decreasing sensor signal. The reaction scheme is as follow⁹⁾:

4. Conclusion

In summary one can conclude that hetero structure of Ti/Pt annealed at 800°C is suited to significantly stabilize FG-FET based hydrogen sensor. The sensor can detect H₂ in concentration range between 0.3% and 2%. The sensor offers high sensitivity, reproducibility, longterm stability and negligible base line change at a temperature range from room temperature to 135°C under dry and wet conditions with response time (t_{90} ~43.2 second). Furthermore, the sensor is more stable with increasing temperatures compared to Ti/Pt based hydrogen sensor. The annealing temperature and time will affect the performance and morphology of the film. This effect will be discussed in a separate paper.

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