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Highly Sensitive MISFET Sensors for Detecting CO Gas Using Porous Platinum and Tungsten Oxide Thin Films

Hisashi Fukuda, Ryuji Zohnishi and Shigeru Nomura
Department of Electrical and Electronic Engineering, Faculty of Engineering, Muroran Institute of Technology, 27-1 Mizumoto-cho, Muroran-shi, Hokkaido 050-8585, Japan
Phone:+81-143-46-5549, Fax:+81-143-46-5501, E-mail:fukuda@mmm.muroran-it.ac.jp

1. Introduction

Monitoring devices for carbon monoxide (CO) play an important role in efforts to improve air quality because CO gases are typical air pollutants released upon combustion of final fuels and biomass burning. It has been reported that the catalytic properties of noble metals (Pd, Ag, Au, Pt etc.) in the metal-insulator-semiconductor (MIS) structure have been used for gas detection applicable to solid-state gas sensors [1-5]. Gas detection based on this technique relies largely on the measurable property change in the solid, such as a change in conductivity attributed to gas adsorption/reaction on the solid surface of a MIS structure, or a change of the metal work function in the Schottky diode and/or MIS field-effect transistors (MISFETs) induced by a catalytic reaction on the solid surface. In recent years, further development of these gas sensors has resulted in the integration of catalytic metals (Pt, Pd or Ag) and metal oxides such as TiO_2 and SnO_x to allow the detection of flammable gases.

In this paper, we have proposed for the first time a novel gas sensing device having sensing materials including a porous Pt onto tungsten oxide (WO_3) thin film structure. The porous Pt/WO_3 multilayer structure was applied as the gate electrode of the MISFET gas sensor. The main focus is on the CO gas-sensing characteristics, and the mechanism of gas-detection behaviors are also discussed.

2. Experimental

The starting materials were boron-doped (1-2 Ω cm) Czochralski (CZ)-grown (100) silicon wafers, which were cut into 1.5 cm × 1.5 cm squares. The devices were fabricated by use of a n-MOS fabrication process. First, a 500-nm-thick field-oxide film was formed on the Si. The source and drain regions were then formed by solid phase diffusion. A 15-nm-thick gate SiO_2 film was formed in dry oxygen ambient at 900℃ for 10 min. A WO_3 layer was formed using 0.5 mol/l solution of $W(CO)_4(Et_2\text{-en})$ by spin-coating onto the gate oxide film. The WO_3 film was heated at 600℃ for 1 hour in oxygen ambient. A porous Pt layer was formed by dropping an ethanol solution containing 0.5 wt% hexachloroplatinic (IV) acid onto WO_3 layer, then heating at 300 ℃ for 10 min in hydrogen ambient.

The schematic drawing of the MISFET sensor is shown in Fig.1. The MISFET had a gate length and gate width of 30 μm and 2.25 mm, respectively.

All electrical measurements of the sensing devices were performed in a vacuum desiccator. CO gas was introduced into the desiccator using a syringe at concentrations ranging from 0 to 1000 ppm.

3. Results and Discussion

Figure 2 shows a scanning electron microscopy (SEM) image of the top Pt film surface. It is clearly seen that the Pt (white part) surface is in the form of islands and shows the agglomeration of roughly spherical particles of 1 μm in size. Figure 3 shows the X-ray diffraction (XRD) patterns of the underlying WO_3 films annealed at 400-900 ℃. The XRD pattern of the sample annealed at 400℃ showed no peaks, indicating the amorphous nature of the films. It is confirmed that the WO_3 films annealed above 500℃ exhibits n-type behavior and is well crystallized with XRD peaks from the (020), (111), (121), (140) and (420) orientations.

Figure 4 shows the drain current versus drain voltage, I_d-V_d characteristics at a the gate voltage of 3 V for different CO concentrations. As shown in this figure, the saturation drain current, I_{dsat}, increases with increasing CO concentration. It was possible to detect 54 ppm of CO gas with a response time of less than 1 min. Subthreshold characteristics, I_d-V_g curves, showed threshold voltage (V_{th}) shifts in the negative bias direction with the introduction of CO gas. The ΔV_{th} versus time with small amounts of CO is shown in Fig.5. The increase of I_{dsat} can be fully explained by the change in the threshold voltage.

We believe that the underlying WO_3 film as a catalytic layer plays the major role in adsorbing CO gas. In fact, no V_{th} change is observed in the MISFET without WO_3 film. Some of the adsorbed molecules on the Pt surface diffuse rapidly into the Pt/WO_3 interface, where the reaction of CO molecules leads to the creation of dipole moments and changes in work function owing to the reduction process of WO_3, thus directly shifting the threshold voltage. The consequent change in voltage across the dipole layer can be expressed as $\Delta V_{th}=-N\vartheta\mu/\varepsilon$, where N is the density of the adsorption site, ϑ is the fractional coverage of adsorped CO, μ is the dipole moment, and ε is the permittivity. By using porous Pt film, the adsorption site is about 100 times larger than that of an unmodified Pt surface. Thus, higher sensitivity is obtained for a porous Pt-WO_3 gate MISFET sensor in spite of relatively lower operating temperature.

4. Conclusion

We have demonstrated for the first time the operation of a novel porous Pt-WO_3 gate MISFET sensor for the detection of carbon monoxide gas. The good response shows that the device can be used as a sensitive detector in a much lower temparature range than that of conventional solid-state gas sensors. The device detection mechanism presented, of this device, is in good agreement with the experimental data.

Ackowledgement

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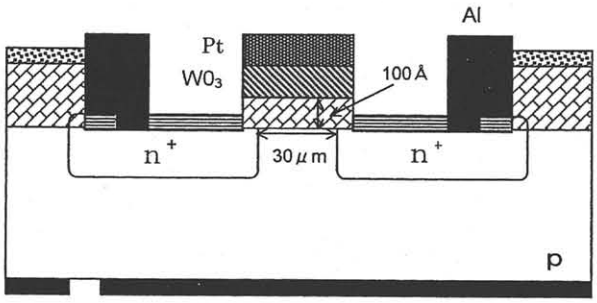

Fig.1 Cross sectional veiw of the MISFET sensor.

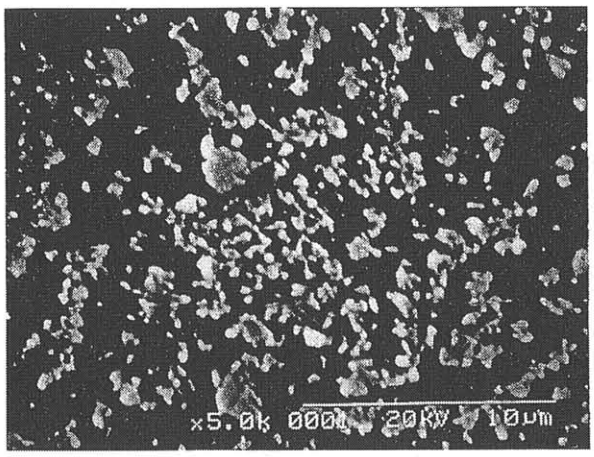

Fig.2 Surface of porous Pt gate of MISFET sensor imaged by SEM.

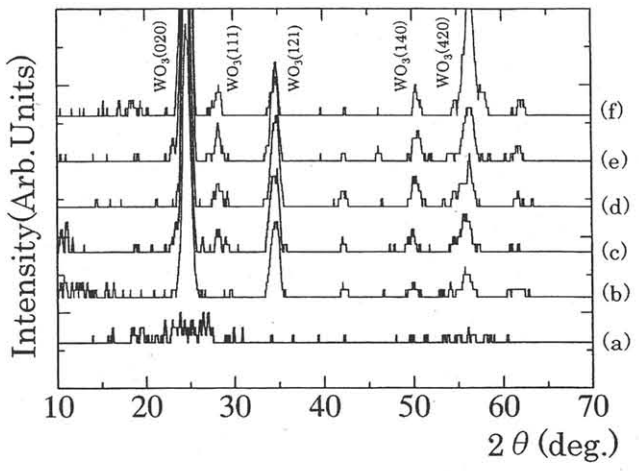

Fig.3 XRD patterns of the WO_3 films annealed at (a) 400℃, (b) 500℃, (c) 600 ℃, (d) 700℃, (e) 800 ℃, (f) 900℃.

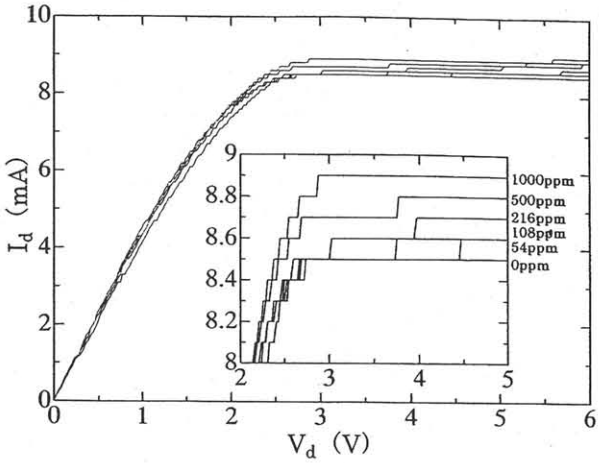

Fig.4 Typical I_d-V_d characteristics at a fixed gate voltage (V_g) of 3 V for different CO concentrations.

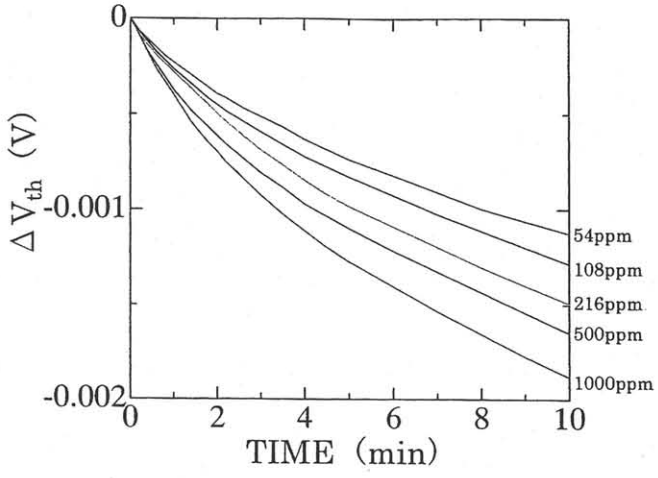

Fig.5 Change in the threshold voltage as a function of time at different CO concentrations during operation at 75℃.