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Highly Sensitive MOSFET Gas Sensors with Porous Pt-SnO_x Gate Electrode for CO Sensing Applications

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1. Introduction

Monitoring devices for carbon monoxide (CO) control play a fundamental role in efforts to improve air quality because CO gases are typical air pollutants released upon combustion of final fuels and biomass burning. It is well known that a noble metal and metal-oxide-semiconductor (MOS) structure have potential gas detection capabilities applicable to solid-state gas sensors [1-3]. Gas detection by 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 MOS structure, or a change of the metal work function in the Schottky diode and/or MOS field-effect transistors (MOSFETs) 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 tin oxide (SnO_x) to allow the detection of O_2, CO and NO gases [1,2]. Another approach is the integration of additives such as antimony (Sb) and/or Pt in SnO_x film [3]. Thus, surface modifications have the potential in order to improve the sensor performance such as the sensitivity, response time and the operating temperature.

In this paper, we have proposed a novel gas sensing device having sensing materials including a porous Pt onto SnO_x thin film structure. The porous Pt/SnO_x multilayer was applied as the gate electrode of the MOSFET gas sensor. MOSFETs have been used in ultralarge-scale integration (ULSI) technology, and have a transducer function allowing transformation of a gas concentration into an electric signal, and receptor function allowing identification of the type of gases. Therefore, MOSFET gas-sensing devices have the potential for high integration as well as high intelligence. In this paper, the main focus is on the CO gas-sensing characteristics, and the mechanism of gas-sensing behaviors are also discussed.

2. Experimental

The starting materials were boron-doped (1-2 Ωcm) Czochralski (CZ)-grown (100) silicon wafers, which were cut into 1.5 cm × 1.5 cm squares. The devices were fabricated on the silicon wafers. A 500 -nm-thick field-oxide film was then formed on the Si. The source and drain regions were formed by solid phase diffusion. Then a 15-nm-thick gate SiO_2 film was formed in dry oxygen ambient at 900℃ for 10 min. A SnO_x layer was formed using 0.5 wt % solution of SnO_x-containing alkoxide by spin-coating onto the gate oxide film. The SnO_x film was heated at 550℃ for 20 min in nitrogen ambient. The size and density of the Sn particles determined by EDX scanning image were 0.17 μm and $3.2 \times 10^8/cm^2$, respectively. A porous Pt gate electrode was formed by dropping an ethanol solution containing 0.5 wt% hexachloroplatinic (IV) acid onto SnO_x layer, then heating at 300℃ for 10 min in hydrogen ambient. The amount of hexachloroplatinic (IV) acid was controlled to form a porous Pt layer with a thickness of < 100 nm. The fabricated MOSFET had a channel length and gate width of 30 μm and 2.25 mm, respectively.

All electrical measurements of the devices were performed at room temperature (27℃) under dark conditions in a vacuum desiccator. CO gas (standard gas, 99.9%) was introduced into the desiccator using a syringe, at concentrations ranging from 0 to 1000ppm.

3. Results and Discussion

Figure 1 shows the typical drain current against drain voltage (I_d-V_d) characteristics of the MOSFET sensor at a fixed gate voltage (V_g) 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 shifts in the negative bias direction with the introduction of CO gas. Threshold voltage change (ΔV_{th}) versus time with small amounts of CO is shown in Fig.2. These experiments show that V_{th} of the transistor decreases in the presence of CO. In addition, ΔV_{th} seems to saturate with increasing exposure time. We believe that the device functions in the following way: CO is adsorbed at the outer part of the porous Pt surface. Some of the adsorbed molecules diffuse rapidly into the Pt/SnO_x interface, where the CO molecules donate electrons to the conduction band of SnO_x and become chemisorbed CO^+ ions. Then, the chemisorbed CO^+ ions create a dipole double layer at the Pt-SnO_x interface.

The change in voltage across the dipole double layer leads to a shift of V_{th} in the negative gate bias direction. In the I_d-V_d characteristics, I_{dsat} can be expressed as [3],

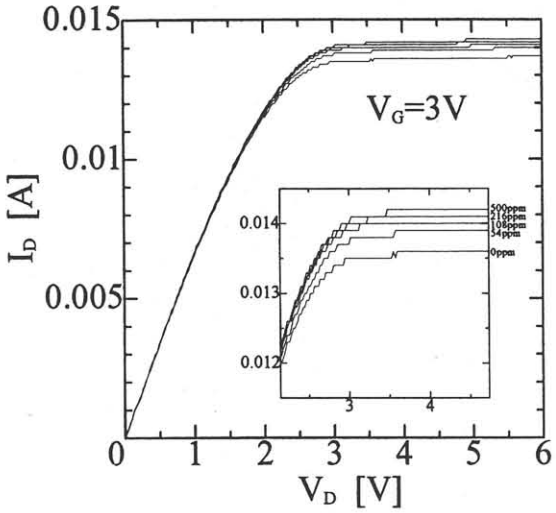

Fig.1 Typical I_d-V_d characteristics of the MOSFET sensor at different CO concentrations during operation at 27℃.

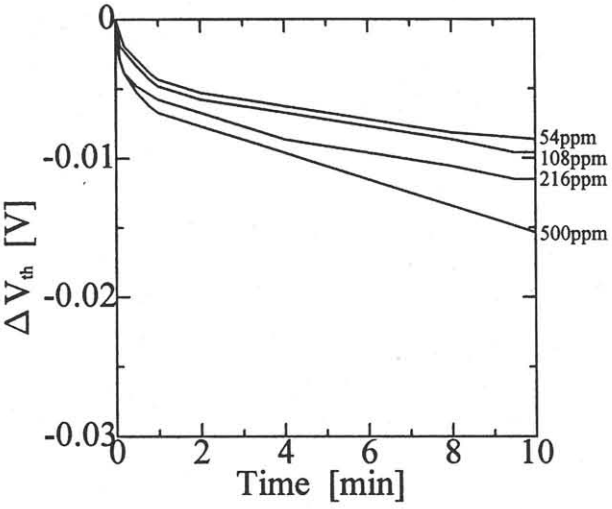

Fig.2 Change in the threshold voltage as a function of time at different CO concentrations during operation at 27℃.

$$I_{dsat} = C\,(V_g - \Delta V_{th})^2/2 \quad (1)$$
$$\Delta V_{th} = -N\theta\mu/\varepsilon, \quad (2)$$

where C is a constant determined by the device design, N is the density of the adsorption site, θ is the coverage of CO at the interface, μ is the dipole moment of the dipole layer, and ε is the permittivity. We have confirmed that ΔV_{th} of a porous Pt-gate MOSFET for hydrogen adsorption is about 10 times larger than that of an unmodified Pt-gate MOSFET. It is attributed to the fact that the density of the adsorption site, N, in porous Pt is much larger than that in the unmodified Pt surface.

The physics of the gas-sensing mechanism can be analyzed by considering the following reaction kinetics at the Pt/SnO_x interface of the MOSFET sensor.

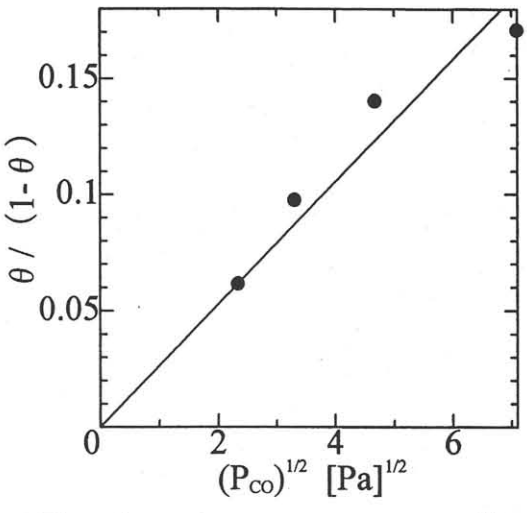

Fig.3 The plots of θ/(1-θ) versus $(P_{CO})^{1/2}$ for a steady state.

$$S + CO\,(g) \underset{d1}{\overset{c1}{\leftrightarrows}} CO^+ + e \quad (3)$$

Where, c_1 and d_1 are the adsorption and desorption rate constants, S represents a surface adsorption site for CO at the Pt/SnO_x interface, CO^+ is the chemisorbed CO ion, and e is the electron given to the conduction band of SnO_x. The coverage, θ, of CO molecules at the interface is given by

$$\theta/(1-\theta) = (c_1 P_{CO}/d_1)^{1/2} \quad (4)$$
$$\theta = \Delta V_{th}/\Delta V_{th(max)}, \quad (5)$$

where $\Delta V_{th(max)}$ is the maximum threshold voltage shift (obtained from extrapolations to $P_{CO}=\infty$). Fig. 3 shows θ/(1-θ) against $(P_{CO})^{1/2}$ at a steady state, where $(c_1/d_1)^{1/2}$ is obtained from the slope of the plots. It is observed that all data are in good agreement with the gas sensing mechanism.

4. Conclusion

We have shown the operation of a new porous $Pt\text{-}SnO_x$ gate MOSFET gas sensor for the detection of carbon monoxide. The good response shows that the device can be used as a sensitive detector in a much lower temparature range (27℃) 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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