Oscillation in a SnO_2 Semiconductor Gas Sensor Exposed to Benzyl Alcohol

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The oscillatory phenomenon in a SnO_2 semiconductor gas sensor exposed to benzyl alcohol vapor is reported. The rhythmic oscillation of sensor conductance maintained for 2 h, and the amplitude and frequency changed depending on the sensor temperature and the concentration of benzyl alcohol vapor. The existence of two different stationary conductance levels depending on the sensor temperature plays an important role in this oscillation.

Over the past few decades, there has been considerable interest in oscillatory phenomena in several gases on solid surfaces.[1–8] Among these, the oscillation in the oxidative reaction of CO on a Pt surface may be the most typical experimental system.[1–4] Ertl and co-workers reported CO oscillation with a clean single crystal surface of Pt.[3,4] It has become clear that the phase transition between the reconstructed (hex) phase and the nonconstructed (1×1) phase is the most essential process for inducing oscillation, at least under isothermal conditions. Nitta and co-workers observed rhythmic oscillation in electric conductance when a gas sensor with n-type SnO_2 was exposed to CO or H_2.[5,6] The mechanism of CO oscillation with an n-type semiconductor was reported with regard to a narrow region in the boundary between SnO_2 grains.[5–8] However, oscillatory phenomena were observed for only a few kinds of gases (CO and H_2). This means that the conditions for sustained oscillation are experimentally limited, i.e., it can be difficult to generate the two stationary states and bifurcation that are necessary for oscillation among gases ($CO + O_2$) on a solid surface (SnO_2).

In this study, we observed long-term oscillation with a SnO_2 gas sensor exposed to benzyl alcohol vapor. By chance, we found the rhythmic oscillation of sensor conductance maintained for 2 h, and the amplitude and frequency changed depending on the sensor temperature and the concentration of benzyl alcohol. The oscillatory region and the two stationary states of conductance were confirmed by changing the sensor temperature. We propose a mechanism for this oscillation that involves coupling between the reaction of benzyl alcohol, including adsorption/desorption, and the temperature of the SnO_2 sensor surface.

DC voltage was generated with a waveform generator (NF Electronic Instruments, WF1946, Japan) and supplied to the heater of a semiconductor sensor.[7] The electric conductance of a semiconductor gas sensor was measured with a digital multimeter (Yokogawa 7552, Japan) and then stored in a personal computer. A SnO_2 gas sensor was used as the semiconductor gas sensor (TGS2620, Figaro Engineering Inc., Osaka, Japan).[9] Benzyl alcohol (0.5 mL) was introduced in a glass cell (40 mL) and the temperature of the cell was maintained at 323 ± 1 K in a water bath (Yamato BF-21, Japan). At this temperature, the concentration of benzyl alcohol was calculated to be 2000-ppm according to the Clausius–Clapeyron equation. Ambient air was purified through columns composed of silica gel, activated carbon, and $CaCl_2$ to remove excess water vapor and other impurities, and this purified air was used as a control. The surface temperature of the gas sensor was measured with an infrared thermometer (Keyence, IT2-01, Japan).

Figure 1 shows the time-variation of the sensor conductance for 2000-ppm benzyl alcohol. When the benzyl alcohol was introduced into the cell ($t = 2$ min), the conductance increased with time. At $t = 4$ min, the conductance reached to 0.5 mS and then oscillation started. Periodic oscillation (period: 33 s) maintained for 2 h, and then the period and amplitude of oscillation gradually increased with time, e.g., the period changed from 40 s at $t = 4$ h to 50 s at $t = 6$ h. Finally, oscillation almost disappeared at $t = 24$ h. The amplitude and period of oscillation increased with the concentration of benzyl alcohol (data not shown). In contrast, no oscillation was observed at a benzyl alcohol concentration lower than 700-ppm under these experimental conditions. In addition, no oscillation was observed when the cell was filled with N_2 in place of purified air.

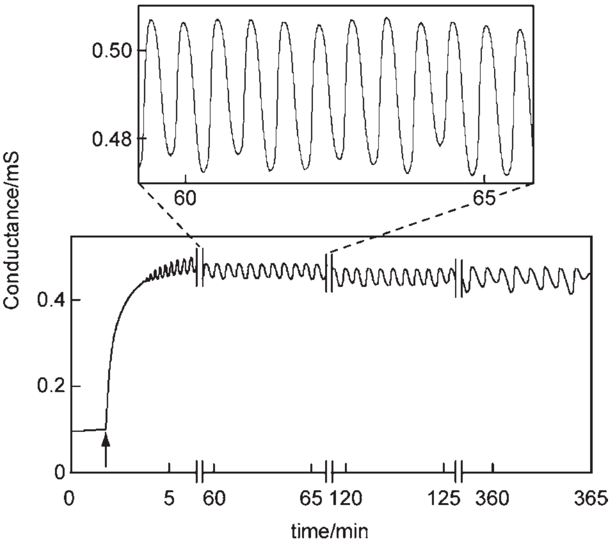

Figure 1. Time-variation of sensor conductance for 2000-ppm benzyl alcohol at a sensor temperature of 500 K. Benzyl alcohol was introduced into the cell at the time indicated by the upward arrow.

Figure 2 shows the dependence of the sensor conductance on the sensor temperature (T_s). Oscillation was observed at 480–520 K. There were two different values of conductance below and above the oscillatory temperature region, i.e., a high conductance value at lower than 470 K and a low conductance value

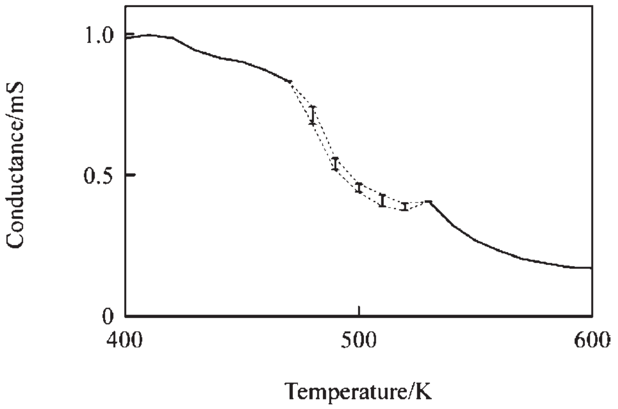

Figure 2. Sensor conductance depending on the sensor temperature, T_s, for 2000-ppm benzyl alcohol. In this experiment, T_s was increased from 400 to 600 K at $dT_s/dt = 0.03\,K\,s^{-1}$. The difference between the maximum and minimum conductance values in the oscillatory region is the amplitude of oscillation.

at higher than 530 K. In addition, the amplitude of oscillation changed depending on T_s in the oscillatory region.

On the basis of these experimental results and referring to related work on the semiconductor system,[9] we suggest a possible mechanism of benzyl alcohol oscillation, as schematically illustrated in Figure 3. The conductance of a SnO_2 gas sensor has been well considered as a model of barrier limited conductance.[9] Two stationary states are needed to generate oscillation.[10] In this system, two stationary conductance values exist below and above the oscillatory region depending on the temperature, and the bifurcation seems to be supercritical, because hysteresis on the scanning of temperature was not observed. The high conductance at the lower sensor temperature, which corresponds to **State I**, suggests that benzyl alcohol may change the barrier potential of the conductance band.[9] The increase in conductance (solid line in Figure 3) may correspond to the diffusion and adsorption of benzyl alcohol on the SnO_2 surface. The electron in ionosorbed oxygen becomes free because of the adsorption of benzyl alcohol and then can then readily move to the conduction band, i.e., the sensor conductance increases. In addition, the oxidation of benzyl alcohol may occur simultaneously, and, therefore, the concentration of ionosorbed oxygen decreases. The product, benzaldehyde, was identified by GC/MS (JEOL JMS-700, Japan). The concentration of benzyl alcohol and adsorbed oxygen on the sensor surface decreases rapidly with oxidation, and oxygen gas in the bulk phase then can be supplied to the sensor surface because of the high concentration and the significant diffusion for oxygen in comparison with the lower concentration and lower diffusion rate for benzyl alcohol. Thus, the sensor conductance decreases, as indicated in **State II**. **States I** and **II** may alternate repeatedly, and, therefore, the conductance oscillates.

In taste and olfaction, living organisms can detect and quantify chemical stimuli on the basis of the time-dependent nature of oscillation since the excitation and pulse generation in the nerve cells are typically nonlinear phenomena.[10] It may be possible to develop the present system as a sensing device because of the long-term and stable oscillation.[11] We found that the nature of oscillation changed characteristically with the addition of other gases, e.g., propane and ethanol (data not shown), i.e., this oscillatory system may be applicable as a novel type of sensing system that mimics taste and olfaction.

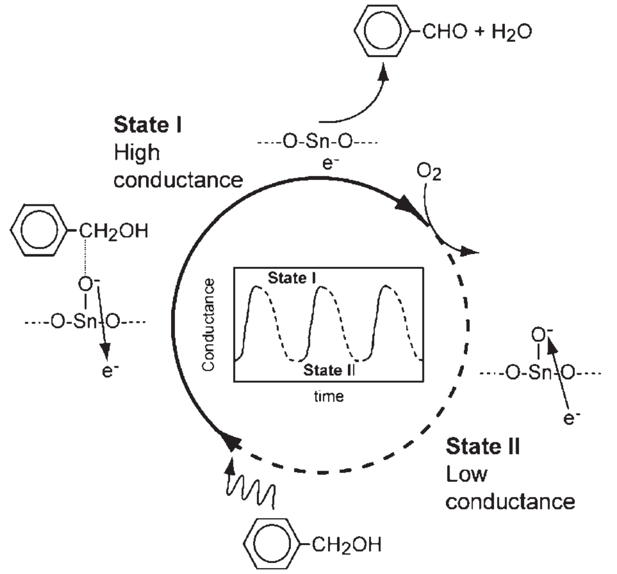

Figure 3. Suggested mechanism of the oscillation in conductance for benzyl alcohol.

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References

1 M. Sheintuch and R. A. Schmitz, *Catal. Rev.—Sci. Eng.*, **15**, 107 (1977).
2 J. E. Zuniga and D. Luss, *J. Catal.*, **53**, 312 (1978).
3 R. Imbihl, M. P. Cox, G. Ertl, H. Müller, and W. Brenig, *J. Chem. Phys.*, **83**, 1578 (1985).
4 R. Imbihl, M. P. Cox, and G. Ertl, *J. Chem. Phys.*, **84**, 3519 (1986).
5 M. Nitta, S. Kanefusa, S. Ohtani, and M. Haradome, *J. Electron. Mater.*, **13**, 15 (1984).
6 S. Kanefusa, M. Nitta, and M. Haradome, *J. Appl. Phys.*, **52**, 498 (1981).
7 S. Nakata, Y. Kato, Y. Kaneda, and K. Yoshikawa, *Appl. Surf. Sci.*, **103**, 369 (1996).
8 R. Ionescu, A. Vancu, and A. Tomescu, *Appl. Surf. Sci.*, **74**, 213 (1994).
9 K. Ihokura and J. Watson, "The Stannic Oxide Gas Sensors, Principle and Applications," CRC Press, Boca Raton (1994).
10 "Chemical Analysis Based on Nonlinearity," ed. by S. Nakata, NOVA, New York (2003).
11 M. C. Wheeler, J. E. Tiffany, R. M. Walton, R. E. Cavicchi, and S. Semancik, *Sens. Actuators B*, **77**, 167 (2001).

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