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Distinction of gases with a semiconductor sensor under a cyclic temperature modulation with second-harmonic heating

Satoshi Nakata *, Hirokazu Okunishi, Yusuke Nakashima

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528, Japan

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Abstract

A gas-sensing system based on a dynamic nonlinear response is reported to improve the selectivity in a sensor response toward sample gases. A cyclic temperature modulation composed of fundamental and second-harmonic heater voltage was applied to a SnO_2 semiconductor gas sensor and the resulting conductance of the sensor was analyzed by fast Fourier transformation (FFT). The dynamic nonlinear responses to hydrocarbons and alcohols were further characterized depending on the phase of the second-harmonic heater voltage (θ_2).

Keywords: Semiconductor; Gas sensor; Nonlinear; Tin dioxide; Cyclic temperature

1. Introduction

An important consideration in the development of chemical sensors is that they should not only rapidly detect a target chemical species but also exhibit high selectivity by eliminating interference, even for an actual sample composed of mixtures or under variable environments. In general, the information obtained from semiconductor sensors is one-dimensional for each detector: the concentration of a certain gas species can be determined by the "dc change" in the resistance (or conductance) of a semiconductor gas sensor, and information on the "temporal axis" is ignored [1–3]. However, most semiconductor gas sensors are not selective enough to detect a single chemical species due to the principle of detection. For example, the sensor responds to most reducing gases, such as hydrocarbons and alcohols, and therefore it is impossible to oxidize only a specific gas in a gaseous mixture for detection.

Thus, one-dimensional information is inadequate for distinguishing between the response to a target and those to other interfering gases. To overcome this problem, a time-dependent sensor response under temperature modulation has been developed [4–18], in addition to the strategy of using sensor arrays [19,20].

We have been developing a gas-sensing system based on the dynamic nonlinear response under a cyclic temperature modulation [21–25] or cyclic diffusion [26] to obtain multi-dimensional information in addition to one-dimensional information under a steady state. We have reported that the nonlinear dynamic response of a gas sensor changes characteristically depending on the concentration and chemical structure of gas molecules, and these characteristic responses can be qualitatively reproduced by a numerical simulation based on the kinetics of gas molecules (diffusion, adsorption, and reaction) on the sensor surface [3,22,23,26].

In this study, we demonstrated that the nonlinear responses to gaseous samples changed characteristically depending on the scanning profile of the cyclic temperature change, which was regulated by the second-harmonic heater voltage, to improve the discrimination of the nonlinear dynamic response. The principle of this system is that the phase of the second-harmonic heater voltage can partially change the dynamic sensor response, which depends on the kinetics of gases on the sensor surface. The dynamic responses of a semiconductor gas sensor under the application of a temperature perturbation including the second harmonic were characterized by the higher harmonics of FFT. These characteristic features of sensor responses to the phase of the second harmonic are discussed in relation to the kinetics on the sensor surface.

* Corresponding author. Tel.: +81 742 27 9191; fax: +81 742 27 9191.
E-mail address: nakatas@nara-edu.ac.jp (S. Nakata).

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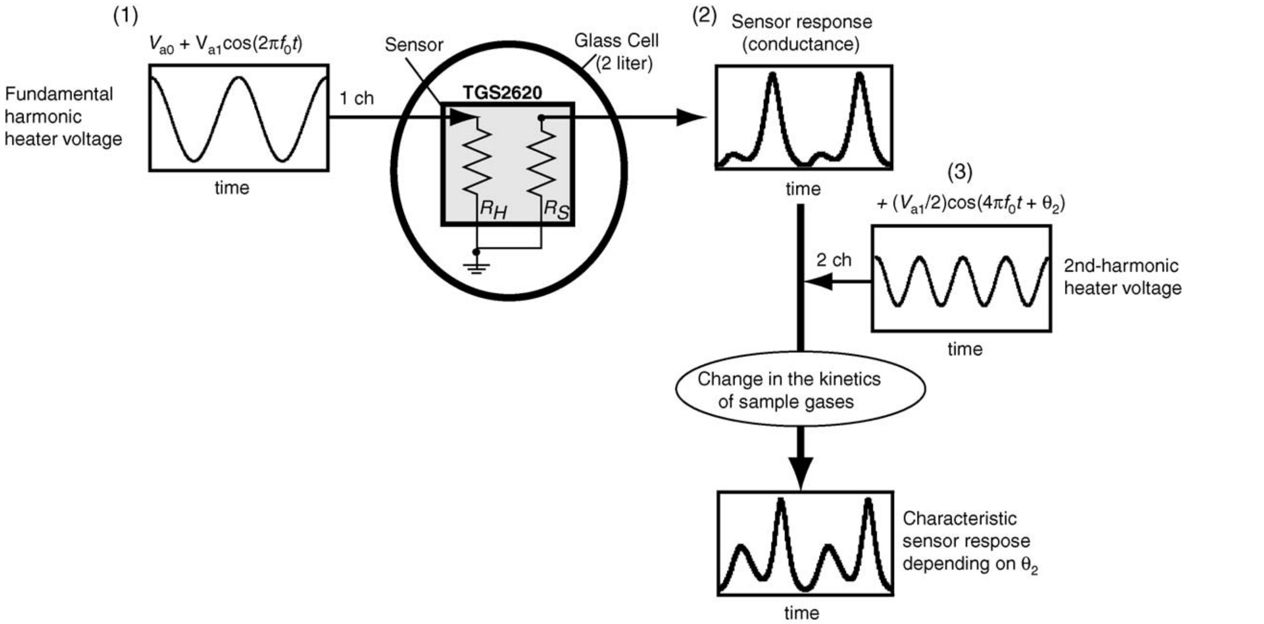

Fig. 1. Diagram of the experimental apparatus for measuring the nonlinear dynamic response (conductance $\propto 1/R_S$) of a semiconductor gas sensor under the different profiles of a cyclic temperature. A modulated voltage composed of the sinusoidal voltage ($f = 0.04$ Hz) on channel 1 (1 ch) and second-harmonic voltage ($f = 0.08$ Hz) on channel 2 (2 ch) for which the phase at $t = 0$, θ_2, was changed, was applied to the heater of the sensor (R_H) to enhance the discrimination of sample gases. The processes (1)–(3) were performed in the present study.

2. Experimental

Fig. 1 shows a schematic representation of the experimental apparatus developed from our previous system, and processes (1)–(3) were performed [21,22,25]. Process (3) was developed in the present study. (1) A fundamental harmonic (frequency: $f_0 = 0.04$ Hz) voltage, V_1 ($=V_{a0} + V_{a1} \cos 2\pi f_0 t$ (V)), was generated with a waveform generator (NF Electronic Instruments, WF1946, Japan) and supplied to the heater of a semiconductor sensor. Under this condition, the time-variation of temperature was almost sinusoidal [23]. (2) The time-developed output signal as the sensor response was characteristically deformed from the sinusoidal input signal of temperature depending on the sample gases, i.e., the sensor response included the higher harmonics which corresponded to nonlinearity. (3) To increase the discrimination of gases based on the dynamic nonlinear response, the second-harmonic ($2f_0 = 0.08$ Hz) voltage, V_2 ($=(V_{a1}/2)\cos(4\pi f_0 t + \theta_2)$ (V)), was applied further, i.e., a modulated signal (V_m), which was composed of the sum of the fundamental and second-harmonic voltages ($V_m = V_1 + V_2$), was supplied to the heater of the gas sensor. The region of sensor temperature was constant at 400–560 K for every θ_2 in V_m, and the amplitude of V_1 was adjusted to be almost twice as large as that of V_2 for a given θ_2 to maintain the same temperature region. Fig. 2 shows representative sensor temperature modulation for (1) $\theta_2 = 0$, (2) $\theta_2 = \pi/2$, (3) $\theta_2 = \pi$, and (4) $\theta_2 = 3\pi/2$. For $\theta_2 = 0$, the scanning rate of temperature was slow around the minimum temperature (T_{min}), while the opposite was true at $\theta_2 = \pi$. For $\theta_2 = \pi/2$, the scanning rate of temperature was slow at $dT/dt < 0$ and fast at $dT/dt > 0$, while the opposite was true at $\theta_2 = 3\pi/2$.

To characterize the dynamic sensor responses to gases, the time-variation of the sensor conductance, for which the sampling

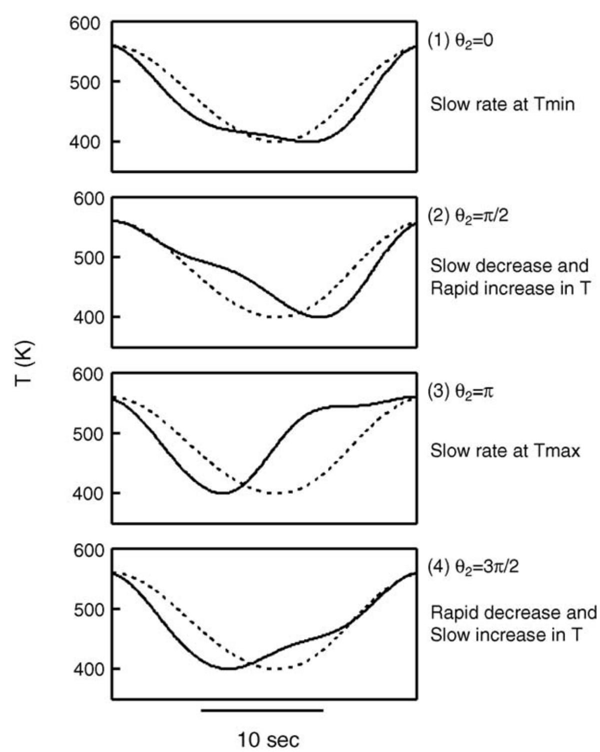

Fig. 2. Experimental results for the time-variation of the sensor temperature under the application of the periodic heater voltage with the second harmonic at θ_2: (1) 0 rad, (2) $\pi/2$ rad, (3) π rad, and (4) $3\pi/2$ rad, and without the second harmonic (dotted line).