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Effect of Temperature on Sensing Behavior in Oscillating Measurements for Doped Tin Oxide Gas Sensor

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The gas sensing behavior in oscillating and static measurements was analyzed. The temperature curves of static and oscillating measurements were compared. Temperature curves under different duty ratios, applied voltages and heating shape were studied. Experimental data showed that the most essential parameter was temperature, because any change in heating voltage and duty ratio resulted in a change in the surface temperature of the sensor element. Further necessary conditions for oscillating measurements are also discussed.

1. Introduction

Selectivity and sensitivity in tin oxide gas sensor can be enhanced using oscillating measurements. A large number of studies have demonstrated that modulation is well known to provide more abundant information than static measurement at a constant operating temperature and also enables us to identify certain gases. In a series of papers beginning in 1991, Nakata and coworkers (1,2) published results of experiments in which a sinusoidal heating voltage was applied to a tin oxide gas sensor. Hiranaka et al.(3) employed pulsed techniques using an applied potential of 5 V to detect an analyte gas. Amamoto et al.(4) constructed a low-power SnO_2 sensor, which was then used in pulse-drive experiments; the response was characteristic of CO, ethanol and hydrogen. Kato et al.(5) applied a 16 ms heating pulse and observed the hysteretic behavior of the sensor output. Again they observed a characteristic response to gases such as CO, methane, n-butane and hydrogen. Kelleter et al.(6) have used the magnitude of the response to voltage pulses applied to a semiconductor gas sensor to calibrate the effects of sensor aging. Eicker(7) distinguished carbon monoxide in a mixture with methane by oscillating the sensor between two fixed potentials. Owen(8) patented a system which cycled the sensor between three fixed potentials and detected CO most sensitively. Advani et al.(9) measured a single gas (H_2S)

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using a square-wave heater voltage. Bukowiecki et al.(10) used a variety of different heater voltage waveforms in an attempt to distinguish between CO, methane, ammonia and hydrogen. A similar research study was performed by Forrster and Strassler.(11) We recently reported rapid detection of pesticide residues using temperature modulation and only a single sensor rather than an array of sensors.(12,13) We also reported the effect of factors such as applied voltage, heating waveform (rectangular, triangular, sawtooth, pulse, sinusoidal, and trapezoidal) and frequency of heater voltage on gas sensing behavior.(14)

Although oscillating measurements have been investigated by many scientists worldwide, most previous studies focus on detection of a specific gas at a constant heating waveform and frequency, and there are few detailed reports on the essential nature of oscillating measurements combined with different heating waveforms and frequencies on oscillating responses. In this paper, we report the differences between static and oscillating measurements, and discuss the temperature variation under static measurement and as a function of duty ratio, applied voltage and heating shape in detail. Finally, we suggest the necessary conditions for oscillating measurements.

2. Experimental

A sol was prepared using a mixed isopropyl alcohol solution of $SnCl_2$, $SbCl_3$, $CaCl_2$ and $SrCl_2$ (purity > 99.5%), which were obtained from the Beijing Chemical Plant (P.R.China). The amounts of Sb, Ca and Sr were fixed at 2.5 mol% as M/Sn (M = Sb, Ca, Sr). As a binder, a given amount of commercial glass powder was added to doped SnO_2 powder calcined at 500°C for 30 min in air. The screen print technique was used to prepare SnO_2 thick films on alumina ceramic substrates with a RuO_2 layer as a heating element on the back. To make the electrodes, platinum paste was painted on both sides of the pellet and the complete structure was annealed at 900°C for 20 min. After aging at a working temperature until a reproducible steady state resistance was achieved, doped SnO_2 thick film gas sensors were obtained.

A volatile gas such as butanone (analytical standard, provided by Sigma-Aldrich Laborchemikalien, Gmbh) was used. The experimental processes are described in detail in ref. 13. Briefly, a headspace sample (HP-7694) was injected into a 2500 ml test chamber in which a single doped tin oxide gas sensor was placed. A circuit board for signal processing made by ECU Electronics Industrial Co., Ltd. (No.38 Research Institute of China Electronics & Technology Group Corp., China) was used. The sensor resistance was monitored, acquired and stored using a PC for further analysis.

3. Results and Discussion

3.1 *Static and oscillating measurements*

A significant difference between the static (the sensor temperature should be held constant with a d.c. heater) and oscillating (the sensor temperature modulated through the oscillation of heater voltage) measurements is shown in Fig. 1. In general, the information obtained from static measurements by chemical sensors is one-dimensional. For example, the change in the resistance of a semiconductor gas sensor (ΔR) or response and recovery time. However, most chemical sensors are not very selective because of the principle of

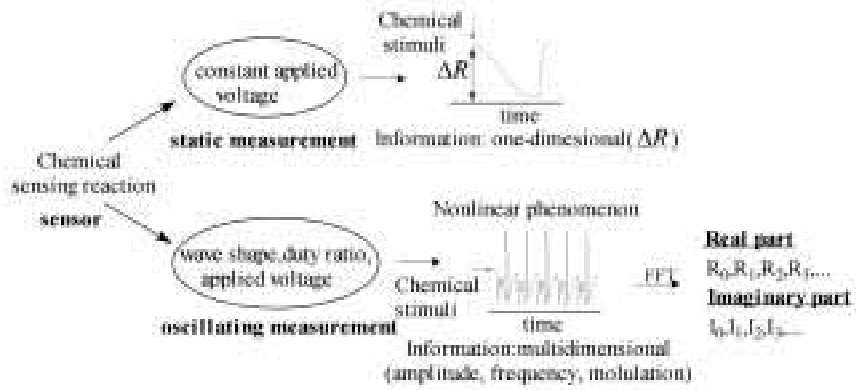

Fig. 1. Difference between static and oscillating measurements.

detection. For example, detection in the semiconductor gas sensor is based on the oxidation or combustion of a gas species. Although several attempts have been made to enhance this selectivity, it is impossible to oxidize only a specific substrate. Instead, we determine how to obtain much more information from molecular recognition using a single sensor. An oscillating system contains abundant information. The key point in this system is the use of nonlinear dynamics in the chemical sensor. The nature of an oscillating system depends on the wave shape of the frequency, duty ratio and applied voltage. We can obtain much useful information about the sensing reaction included amplitude and frequency; it is beneficial to analyze the sensing mechanism for the gases to be tested and to enhance the selectivity. The time trace of the output signal is Fourier-transformed to the frequency domain.(13) The deformation of the output signal compared with the input corresponding to the nonlinearity of the experimental system and is quantitatively evaluated as the higher harmonics of a Fourier transformation. Here, R_n and I_n are the amplitudes of the real and imaginary parts, respectively (R_o: d.c.value of the output signal; R_1 and I_1: the fundamental harmonics). Higher harmonics in a nonlinear system appear with the application of a sinusoidal potential at a single frequency, and no higher harmonics appear in a linear system.

3.2 *Temperature variation under static measurements*

Under an identical heating voltage such as 7 V, in a butanone atmosphere, the temperature variation curves under static measurements are investigated as shown in Fig. 2. The temperature of the doped tin oxide surface has a tendency to vary. Although they have different concentrations, their regularities are similar with increasing concentration; the maximum temperature is enhanced and then it levels out. In addition, the time to reach the maximum temperature increases. Here, the most important observation is that no periodic variation occurs.

3.3 *Temperature curves for different duty ratios*

Figure 3 shows temperature curves on tin oxide sensor surfaces under different duty ratios in 0.5 ppm butanone atmosphere at an applied voltage of 7 V in the rectangular mode; the inset shows the corresponding oscillating behavior. The duty ratio is defined as: $RA = t_h/(t_h+t_l)$, where t_h and t_l are the times required for high-level and low-level, respectively. Obviously, compared with static measurements, the most important difference is that periodic tem-

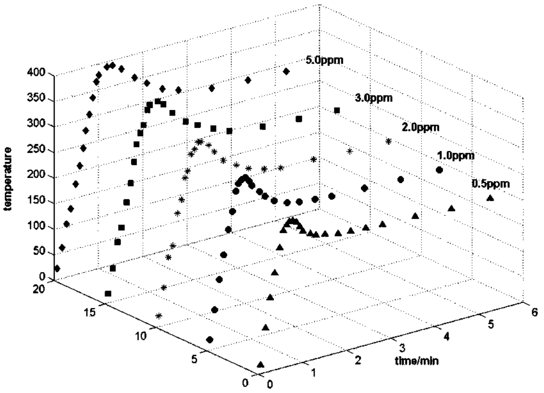

Fig. 2. Temperature curves in butanone atmosphere at constant applied voltage of 7 V.

perature variation can be observed.

Although the shapes describing variations in surface temperature are similar to each other under different duty ratios, it is worth noting that the maximum and minimum temperatures are different. For example, for duty ratios of 5/(5+20), 10/(10+20), 15/(15+20) and 20/(20+20), the corresponding temperature ranges are 72–130°C, 97–186 °C, 115–232°C and 130–276°C; the temperature differences are 58°C, 89°C, 117°C and 146 °C, respectively. Similarly, at a duty ratio of 30/(30+20), the temperature difference reaches 164°C (from 125 to 289°C). Generally, the optimal duty ratio is confirmed on the basis of reaction and detection time. It is also necessary to point out that, although the temperature curves are similar to each other under different conditions, the temperature gradient $\partial T/\partial \tau$ is obviously different, where T and τ are the surface temperature of the sensor and the corresponding time, respectively. The sensors also exhibit much interesting gas sensing behavior (see insert figure). The periodic variation in temperature in an oscillating system has advantages, for example, a cyclic temperature variation can give a unique signature for each gas because of the different rates of reaction of various analyte gases at different temperatures. Periodic shifts to higher temperatures may be required to clean the sensor surface of incompletely oxidized contaminants, which accumulated at low temperatures. The most important advantage is that it avoids the “drift effect” because for each gas there is usually a point temperature or heater voltage in the cycle which corresponds to a maximum in the conductance-temperature profile. This enables the experimental results to have better reproducibility. Thus, the effect of the duty ratio on oscillating behavior may be understood in terms of the differences in surface temperature.

3.4 *Temperature curves under different applied voltages*

To investigate the nature of the effect of applied voltages on sensor oscillating behavior, the relative intensities of surface temperature under different applied voltages are reported in Fig. 4. From the previous discussions, it is worth emphasizing that the higher the applied voltage, the less obvious the “hysteresis effect” of temperature variation on the sensor surface. The “hysteresis effect” is that the sensor surface temperature does not vary in step with the time variation of the duty ratios. Because of the “hysteresis effect,” the oscillating responses are instable at applied voltages of 3 V and 4 V.(14) These data show

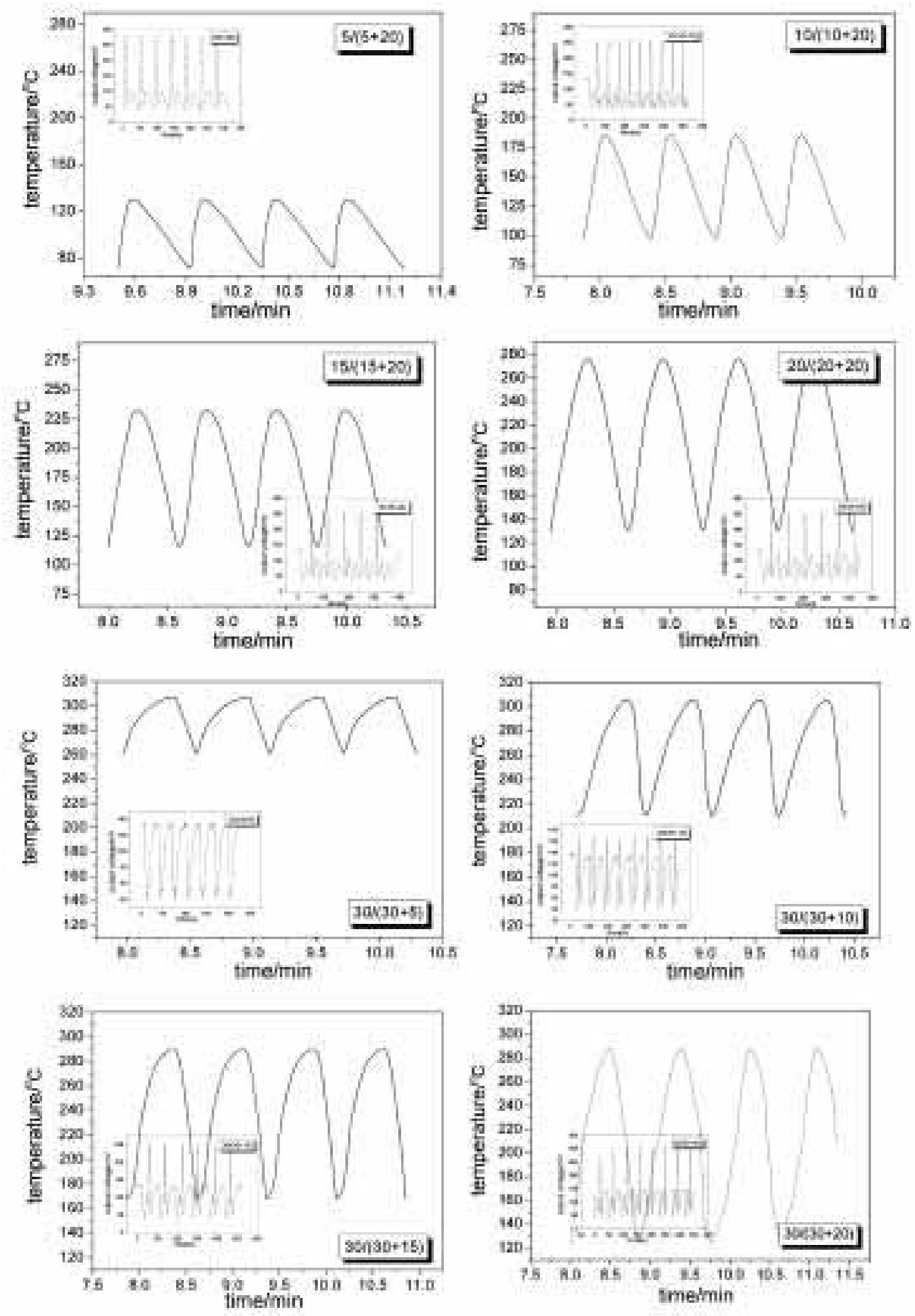

Fig. 3. Temperature curves for difference duty ratios in 0.5 ppm butanone controlling applied voltage of 7 V in rectangular mode. The inset corresponds to an oscillating curve.

that the different voltages result in variations of sensor surface temperature.

The temperature curves for different heating shapes have also been studied. The tendency toward variation is similar to that already mentioned, and the nature of the variation includes different minimum and maximum temperatures, different temperature differences, different temperature gradients $\partial T/\partial \tau$, and other features. Unnecessary details are not given here.

3.5 *Necessary conditions for oscillating measurements*

First, as for the species of sensing materials, only the gas-sensing materials of the surface-controlled type such as SnO_2 and ZnO have a special sensing behavior during oscillating measurements. Sensing materials of the bulk-effect-controlled type such as Fe_2O_3 demonstrate no interesting sensing behavior, although the surface temperature does change when a variable voltage is applied. This may be understood from their different sensing mechanism. Figure 5 shows the energy diagram of various oxygen species in the gas phase, adsorbed at the surface and bound within the lattice of tin oxide. It is widely accepted that the overall surface stoichiometry has a decisive influence on surface conductivity for oxides. Oxygen vacancies act as donors, increasing the surface conductivity, whereas adsorbed oxygen ions act as surface acceptors, binding electrons and diminishing surface conductivity. The energy difference between O^{2-} adsorbed ($O_{ads}{}^{2-}$) and O^- bound to a lattice site ($O_{lat}{}^{2-}$) is estimated to range from approximately 2000 kJ/mol or 20 eV, between $1/2O_{2gas}$ and $1/2O_2{}^-{}_{ads}$ to approximately 140 kJ/mol or 1.5 eV.

For SnO_2 films, the reaction $O_2{}^-{}_{ads}+e^- = 2O^-{}_{ads}$ takes place with increasing temperature. The desorption temperatures of the SnO_2 surface are approximately 823 K for $O^-{}_{ads}$ ions and approximately 423 K for $O_2{}^-{}_{ads}$ ions. At constant oxygen coverage, the transition causes an increase in surface charge density with corresponding variations in band bending and surface conductivity. From conductance measurements, it is concluded that the transition takes place slowly. Therefore, a rapid temperature change in a part of the sensors is usually followed by a creeping change in conductance. The oxygen coverage adjusts to a new equilibrium and the adsorbed oxygen is converted into another species.

The reactivity of $O^-{}_{ads}$ is high and exceeds that of $O_2{}^-{}_{ads}$. $O^{2-}{}_{ads}$ should not be stable if it does not react immediately or is trapped by an oxygen vacancy and stabilized by the

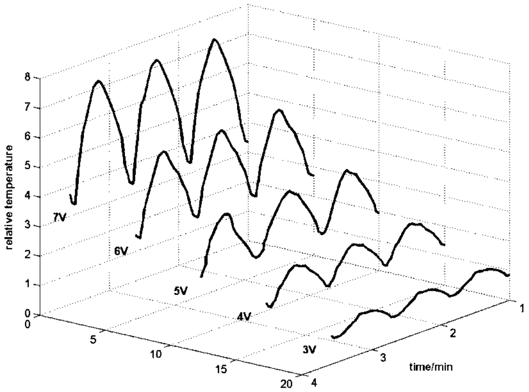

Fig. 4. Relative temperature curves under different applied voltages with squared modulation.

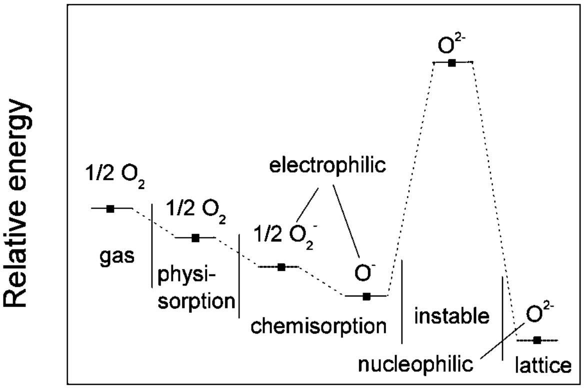

Fig. 5. Energy diagram for various oxygen species in gas phase adsorbed at surface and bound within the lattice of tin dioxide.

Madelung potential of the lattice. With respect to oxidation reactions, the adsorbed O_2^- and O^- species are classified as “electrophilic” reactants, which preferentially attack a C-C bond abstracting electrons, whereas the “nucleophilic” O^{2-} ions bind within the lattice at the surface and react with activated hydrogen or hydrocarbon molecules.(15)

During static measurements, the oxygen adsorbates are partly consumed by oxidation of target gases on the SnO_2 surface. The decrease in the amount of chemisorbed oxygen induces an increase in conductance. In the case of the oscillating mode, when the sensor temperature is modulated with a rectangular heating mode, the complicated response transients are considered to be closely related to different reaction kinetics of individual target molecules on the SnO_2 surface. During the temperature modulation, no equilibrium exists among the surface oxygen species. In this way, reactions between reducing and oxidizing gases are markedly influenced by temperature modulation, and complicated response transients characteristic of individual target molecules result. Thus, the method of oscillating measurement is quite beneficial for the identification of sample gases and analyzing sensing mechanisms.

Second, as for the structure of the sensing element, in general, the structure of the element must be beneficial for heating and radiating, and a smaller volume and thermal capacity are required. The structure includes two types: one is a direct heating type through the test loop; the other is an indirect heating type such as the one investigated. Hard fabrication is required for the latter type. Third, as for the test gas, after reaction with the adsorbed oxygen ions on the surface of the sensing material, easy desorption of the product is required. If an element is also sensitive to a product, it is highly advantageous to analyze the sensing mechanism. As for the concentration of test gas, generally in a certain range of concentrations, with an increase in concentration, the amplitude of the response also increases. In contrast, no interesting oscillation behavior is observed when the concentration is too high. This may be explained as follows: when the concentration increases to a certain extent, the percentage of coverage by the test gas increases instead of the oxygen adsorption on the sensor surface resulting in the termination of oxygen adsorption. Subsequently, the oscillating response disappears even if temperature variations occur on the sensor surface.

4. Conclusions

The study of oscillating and static measurements has demonstrated the advantage of the former in maximizing the information extracted from a single gas sensor. The oscillating measurements are beneficial to the discrimination of gaseous molecules. No periodic temperature variation can be observed under static measurements. The temperature curves exhibit periodic variation under a variety of influencing factors such as applied voltage, duty ratio and heating shape. The effects of the influential factors mentioned may be understood in terms of variations in the surface temperature of the sensing element. As for identical chemical sensors, meanwhile, the changing nature depended on the variability of surface temperature of the sensing element. Further analysis showed that the necessary conditions for oscillating measurements depend on the species of the sensing materials, the structure of the element, the test gas and its concentration.

Acknowledgements

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