Study of Influencing Factors of Dynamic Measurements Based on SnO$_2$ Gas Sensor

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Abstract: The gas-sensing behaviour based on a dynamic measurement method of a single SnO$_2$ gas sensor was investigated by comparison with the static measurement. The influencing factors of nonlinear response such as modulation temperature, duty ratio, heating waveform (rectangular, sinusoidal, saw-tooth, pulse, etc.) were also studied. Experimental data showed that temperature was the most essential factor because the changes of frequency and heating waveform could result in the changes of temperature essentially.

Keywords: Dynamic measurement, gas-sensing behaviour, influencing factors.

Introduction

Presently, low-cost tin-oxide chemical sensors applied to gas detection present some well-known problems (lack of selectivity, drift, etc.) which motivates active research in material science, different measurement strategies and signal-processing algorithms, different measurement strategies including sensors arrays, static and dynamic measurements, etc. Several attempts have been focused on dynamic measurements which include temperature transient or pulsed techniques and temperature modulation through oscillation of heater voltage because they have suggested that temperature modulation of tin-oxide sensor provides more information from a single sensor than static measurement [1-19]. However, these works always focused on the identification of certain gases such as H_2S, CO, NO_2, CO_2, ethanol, methane, n-butane, ethane, propane, propylene, ammonia, and so on under a given constant heating waveform, frequency and operation temperature.

In our previous work, we reported rapid detecting of pesticide residues using temperature modulation by employing only a single sensor rather than an array. We also reported the amplitudes of the higher harmonics of the FFT signal exhibited characteristic changes that depended not only on the species of pesticide gases but also on the concentration of pesticide gases by means of analysis dynamic responses [20, 21].

In the present paper, we will report on the advantages of the dynamic measurement and discuss the influencing factors of nonlinear responses such as modulation temperature, frequency, heating shape waveform (rectangular, triangular, saw-tooth, pulse, sinusoidal) throughout the experimental trails.

Experimental

The sol was prepared using a mixed ethanol solution of $SnCl_2$, $SbCl_3$, $CaCl_2$ and $SrCl_2$. The amounts of Sb, Ca and Sr elements were fixed to 2.5 mol% as M/Sn, respectively. As a binder, a given amount of commercial glass powder was added in doped SnO_2 powder formed by calcinating the powder at 500 °C for half an hour in air. The screen-printing 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. The thick films were sintered at various temperatures for half an hour in air to obtain doped SnO_2 TF gas sensors. These elements were aged in working temperature until reproducible steady-state resistances were obtained.

A headspace sample (HP-7694) was used to inject sample gases measured into a 2500 ml sensor test chamber, where a single SnO_2 gas sensor was kept. Butanone, acetone, ethanol, methanol, formaldehyde and cyclohexanone (Analytical standard, provided by Sigma-Aldrich Laborchemikalien Gmbh) were measured. The signal-producing circuit board was made by ECU Electronics Industrial Co., LTD (No. 38 Research Institute of China Electronics & Technology Group Corp., China). The signal frequency and operating temperatures settings were adjusted to obtain good sensitivities and selectivity to the pesticide gases measured. The sensor resistance was monitored, acquired and stored in a PC for further analysis. Fig.1 shows the experimental set-up. The measurement process was as follows: dry air at a constant flow rate of 10 ml/sec was used as carrier gas. Data acquisition started from 80 s before the injection of the test gases sample into the air-flow. The sampling rate was set to two points per second and it took several minutes to complete the measurements. The surface

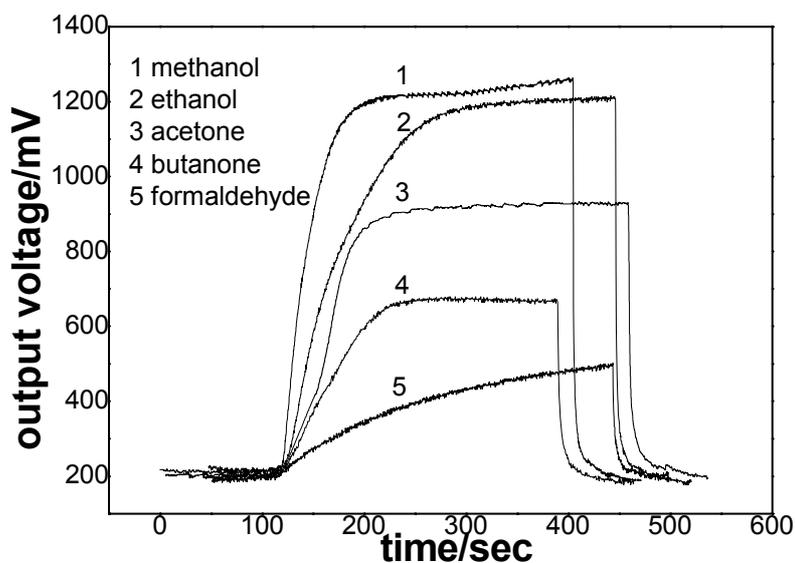temperature of the gas-sensing element was measured with an infrared thermometer (Keyence, IT2-01, Japan).
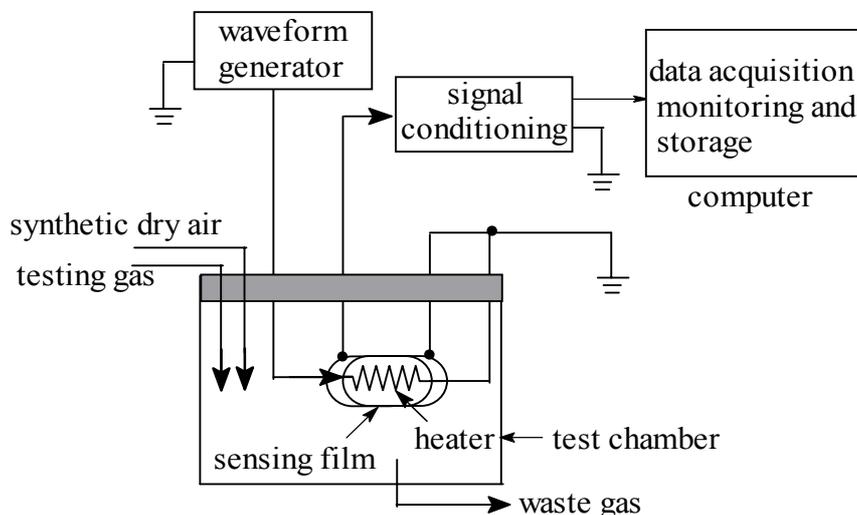
Figure 1. Experimental set-up.

Results and discussion

Static responses of the SnO$_2$-based gas sensor

The static responses to 0.5 ppm butanone, acetone, ethanol, methanol and formaldehyde at 300 °C for the SnO$_2$ sensor are reported in Fig. 2.

Figure 2. Static responses to butanone, acetone, ethanol, methanol and formaldehyde. Experimental conditions: applied potential 7 V, sampling dosage 0.5 ppm.

As shown in the figure, one could clearly observe that the resistance of the sensing element changes obviously upon exposure to the organic gas, meanwhile the response time could be observed audio-visually by means of the tendency of the static curves. It was also necessary to point out that, however, in addition to the changes in resistance and response time, there was no other information about reaction processes, so it was difficult to analyses the sensing mechanism for butanone, acetone, ethanol and methanol. Except the static response to formaldehyde, the other responses were similar to each other. In fact, there are two types of different functional groups (carbonyl group and hydroxyl group). There is no way to distinguish between the carbonyl and hydroxyl group because of the shortcoming concerning their lack of sufficient phenomenon. In a word, during static measurements, only the resistance changes of the sensing element in initial and final state were observed, as for the other changes during reaction processes no other information was obtained.

Dynamic nonlinear responses of SnO$_2$-based gas sensor

Fig. 3 reports the dynamic nonlinear responses to 0.5 ppm ethanol, methanol, formaldehyde and cyclohexanone of a single SnO$_2$ gas sensor, respectively. Experimental conditions were as follows: applied potential 7 V, modulation frequency 20 mHz, rectangular mode.

Firstly, as seen in Fig. 3, it was worth to note that there was sufficient reaction information in the dynamic nonlinear responses, so the sample gases could be easily identified by means of different nonlinear responses. In the four selected species, there are three types of different functional groups (hydroxyl group, aldehyde group and ring ketone); one could easily obtain the distinguishing and connection among the testing species by comparison the static responses. In the case of the dynamic responses to ethanol and methanol, because of their identical hydroxyl group, there is a similar tendency in the curves.

Secondly, it was widely accepted that oxygen in air could be chemisorbed and decomposed as O_2^-, O^- and O^{2-}. At a constant temperature, there existed an equilibrium state at the surface of the SnO$_2$ sensing material: $O_2 \leftrightarrow O_2^-(ad) \leftrightarrow O^-(ad) \leftrightarrow O^{2-}(ad)$. Semiconductor gas sensors monitor changes in the conductance during the interaction of a chemically sensitive material such as SnO$_2$ with molecules to be detected in the gas phase; the reaction steps involved the low-temperature surface reactions and secondly, involved the high-temperature bulk reactions between point defects in the SnO$_2$ crystal and oxygen (O_2) in gas phase. The first step was adsorption and catalytic reactions at active sites (the latter involves intrinsic point defects such as oxygen vacancies and/or extrinsic point defects, like segregated metal atoms) and similar reactions at grain boundaries or at three-phase boundaries (e.g., at metallic contacts on surface metallic clusters). All of these reactions involved adsorbed negatively charged molecular (O^{2-}) or atomic (O^-) oxygen species as well as hydroxyl groups (OH) at different surface sites.
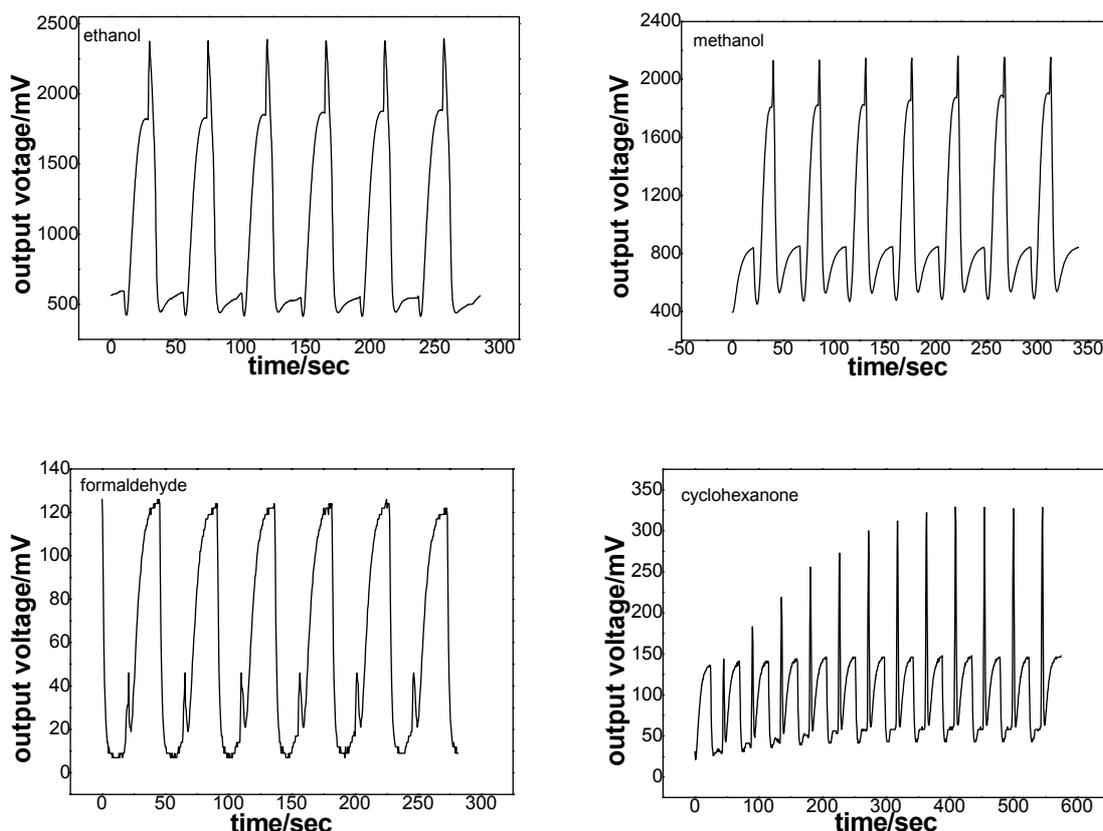
Figure 3. Dynamic nonlinear responses to ethanol, methanol, formaldehyde and cyclohexanone. Experimental conditions: sampling dosage 0.5 ppm, applied potential 7 V, modulation frequency 20 mHz, rectangular temperature mode.

During the static measurement processes, the adsorbed oxygen results in oxidation of testing gases on the surface and in a decrease of the chemisorbed oxygen concentration, inducing an increase of the conductance. As seen from Fig. 3, it was found that gas identification in a rectangular temperature-modulated mode was related to the different reaction kinetics of the interacting gases on the tin-oxide surface. It is clear that, by temperature modulation, it became possible to provide the surface oxygen species at constant temperatures at which, in equilibrium conditions, they would not exist. In this way, the reaction with the reducing and oxidizing gases was dramatically influenced, e.g. at lower temperatures and at higher temperatures the responses to sample gases exhibited their characteristic wave shape due to the reaction with different oxygen species. So, from the above mentioned, we suggested that the dynamic nonlinear responses are beneficial to analyse the sensing mechanism of the sample gases.

Thirdly, it was also found that the operation temperature during the dynamic processes was lower than that of the static processes. For example, the static operation temperature using an applied potential of 7 V reaches 450 °C, whereas the dynamic temperature at operation frequency of 20 mHz was in the range of 300~210 °C.Therefore, we suggested that a modulated temperature operation mode not only enhances the selectivity of a gas sensor but also reduces the overall power consumption.

Effect of the modulation temperature at frequency of 20 mHz
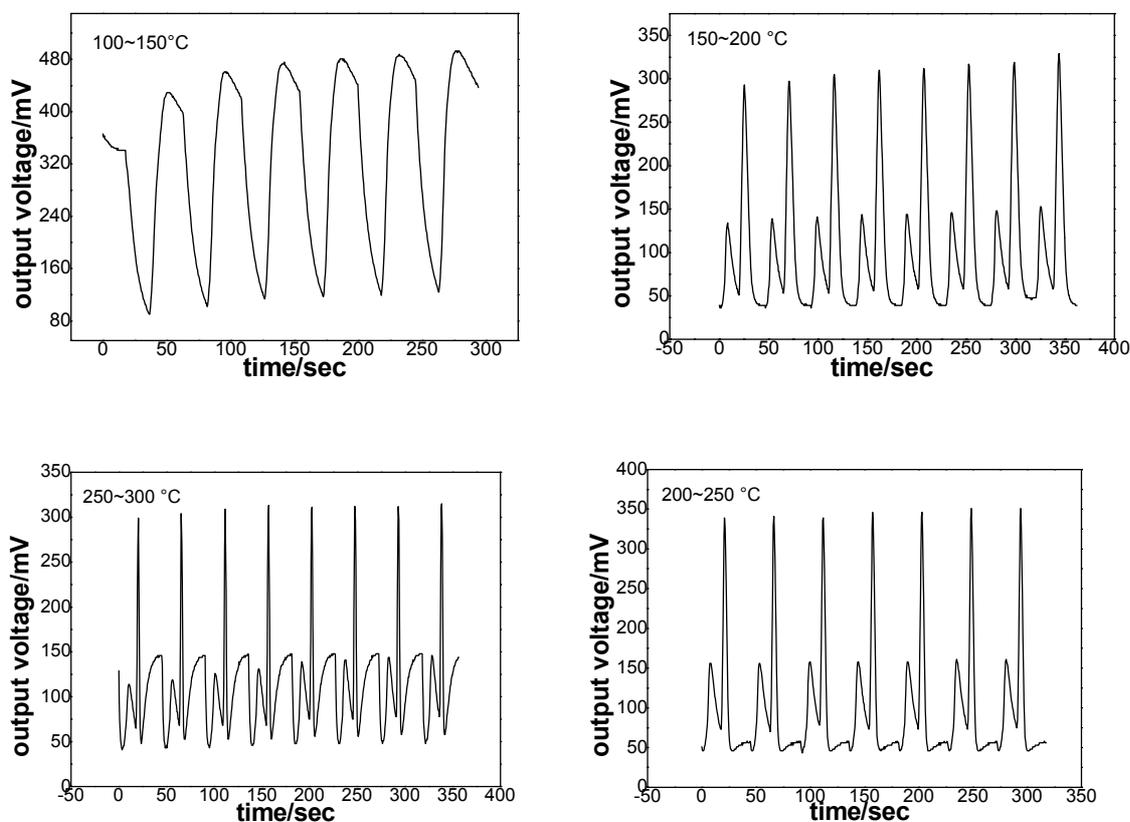
Figure 4. Effect of temperature on the responses of 0.5 ppm acetone at a frequency of 20 mHz in a rectangular mode.

To optimize the selectivity of the temperature-modulated sensor, it was necessary to obtain a relationship between a given temperature and its conductance response in the presence of a specific gas. Fig. 4 reports the effect of a given temperature on the responses of 0.5 ppm acetone at a constant frequency of 20 mHz in a rectangular mode. As seen in the figure, the different responses at different operation temperatures could be easily observed. This case noted that the sensor exhibited an enhanced selectivity to acetone with increasing temperature. It was suggested that acetone can be identified by means of a relatively complete response between 250 °C and 300 °C. Obviously, there were different surface reaction mechanisms between acetone and chemisorbed oxygen at different given operation temperatures.

Effect of the duty ratio at an applied potential of 7 V

Fig. 5 clearly shows the time-dependent change shape of the resistance of the sensor in the presence of butanone in air at different duty ratios by controlling an applied potential of 7 V in a rectangular mode. As seen in the figure, one can easily observe the effects of electrical outage and switch-on on the dynamic responses. In the left part of the figure, the lower half of the response was influenced evidently by the state of switch-on electrical current. With the lengthening of the switch-on time (electrical outage time in thermal cycle), the response was appeared gradually. Inversely, the upper half of the response was influenced obviously by the state of electrical outage; the more the time of the electrical outage, the more evident the upper half of the response. Therefore, the duty ratio was beneficial to investigate the sensing mechanism, and it was in agreement with the analysis in the dynamic nonlinear response.
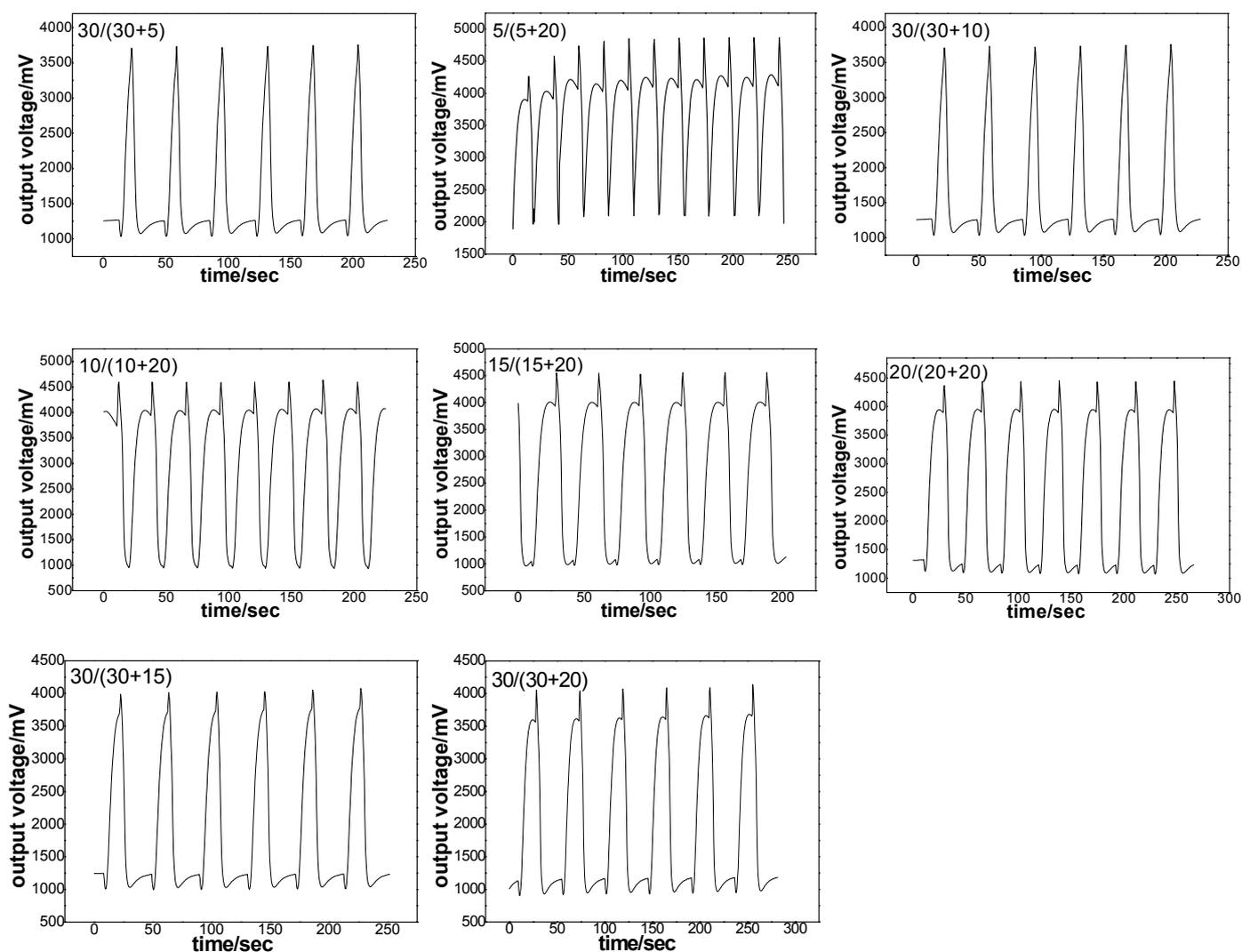
Figure 5. Effect of duty ratio on the responses to ethanol at an applied potential of 7 V in a rectangular mode.

Effect of modulation waveform
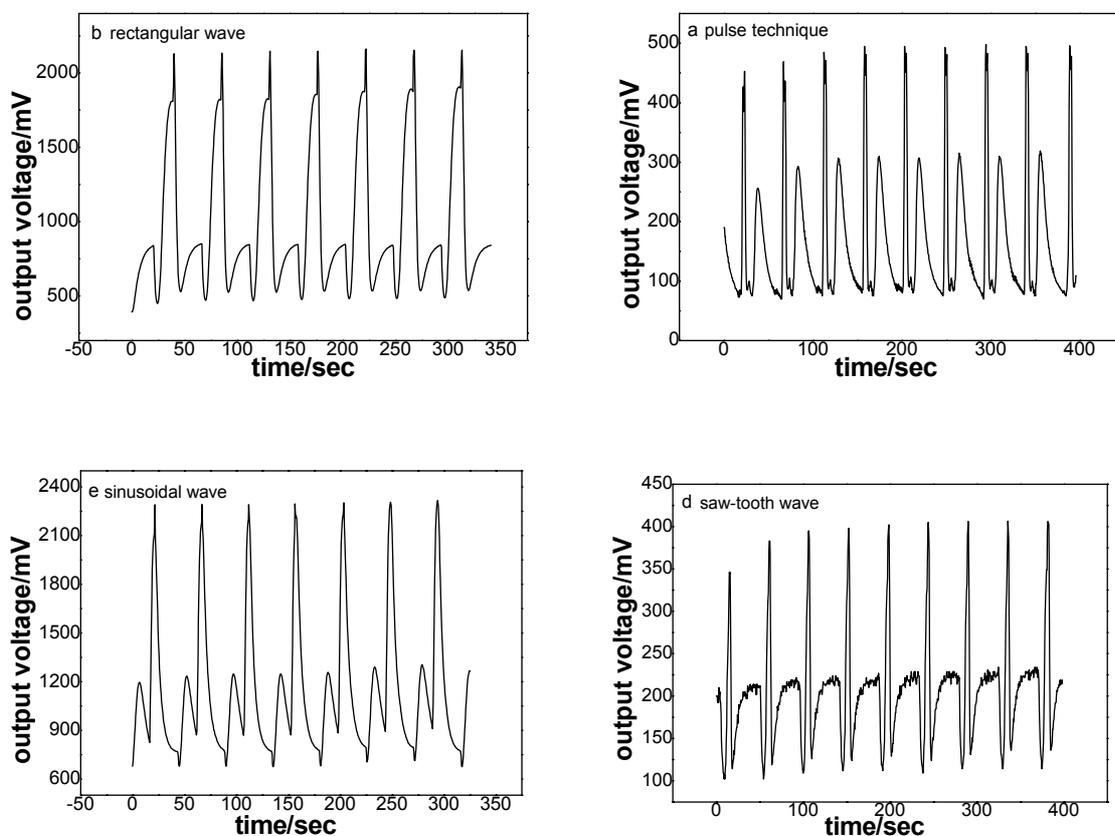
Figure 6. Effect of modulation waveform on the dynamic response of methanol. Experimental conditions: applied potential 7 V, modulation frequency 20 mHz.

In order to improve the detection, the modulation of the wave shape was carried out. The dynamic nonlinear responses to methanol are reported in Fig. 6 using different modulation waveforms. Although the object was commentarial, one could see that the nonlinear responses were different to each other. These experimental data are in agreement with A. Ortega's report. A. Ortega and his co-workers have reported that CO and CH_4 could be detected by using pulse and triangular heating waveforms [7]. According to the analysis of the sections above, the change of the heating shape waveform had influence on the sensing behavior of the testing gas by means of the change of the sensing element's surface temperature.

Conclusions

The study carried out over the dynamic and static measurements has allowed to demonstrate the advantage of the former measures in order to obtain the maximization of the information extracted from a single gas sensor. Experimental test showed that the dynamic measurement was beneficial to facilitate the feature extraction algorithm as the most significant output signal to separate the testing gases. Meanwhile, a variety of influencing factors such as modulation temperature, duty ratio, heating

shape waveform (rectangular, saw-tooth, pulse, sinusoidal) were investigated. It was found that the characteristic optimum oxidation temperatures of acetone were 250~300 °C at a frequency of 20 mHz. At a frequency of 20 mHz, the temperature contrast reached a maximum which was beneficial for detecting butanone. Experimental data also showed that different waveforms could improve the detection if the separation of certain gases is not clear. Finally, all data showed that temperature was the most essential influencing factor.

Acknowledgments

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