第 21 卷 第 5 期
2008 年 5 月

传 感 技 术 学 报
CHINESE JOURNAL OF SENSORS AND ACTUATORS

Vol. 21 No. 5
MAY. 2008

Oscillating Behavior of Tin Oxide Gas Sensor and Its Application for Pesticide Residues Determination *

LIU Tie-bing *, *SHAO Dong-liang*, *SHEN Qing*, *JIANG Jun-shu*, *YAO Yan-ru*, *WU Qi-lu*

(National Center of Agricultural Standardization and Inspection, Hefei 230051, *China)*

Abstract: It introduced that M(Sb, Ca, Sr) was added to doped SnO_2 and the principle of device detected pesidicide residues. The oscillating behavior of a single tin oxide gas sensor was investigated by comparison with the static measurements. The factors influencing oscillating behaviors such as applied potential, duty ratio, and applied potential waveform (rectangular, sinusoidal, saw-tooth, pulse, and others) were also studied. Experimental data showed the dynamic measurements of the oxide tin sensor had been suggested that which could provide more information from a single sensor than static measurements. The organophosphorus pesticide residues such as parathion could be determined by using this oscillating measurement method.

Key words: materials; oxide tin sensor; electrochemistry; oscillating behavior; influencing factors; pesticide residues; determination

EEACC: 7230L

氧化锡气敏传感器动态响应特性用于农药残留检测的研究 *

刘铁兵 * ,邵栋梁,沈 清, 蒋俊树,姚彦如,吴启陆

(国家农业标准化与监测中心,合肥 230051)

摘 要:本文介绍了氧化锡气敏传感器参杂金属(Sb,Ca,Sr)的制备及检测农药残留检测装置的原理,通过对氧化锡气敏传感器,在动态与静态条件下,检测农药残留的响应特征及影响因素进行了研究,如采用电压、占空比、电压波形(矩形波、正弦波、锯齿波、脉冲波)的变化,比较研究了农药残留检测的动态与静态响应特征,结果表明动态的测量方法比静态方法可以得到更多的信息,用这种动态测量方法检测对硫磷等有机磷类农药残留具有良好效果。

关键词:材料学;二氧化锡传感器;电化学;动态响应特征;影响因素;农药残留;检测

中图分类号:TP212.2 **文献标识码**:A **文章编号**:1004-1699(2008)05-0739-05

Currently, although low cost tin oxide gas sensors have been developed previously to achieve high selectivity for a particular chemical species, they also present some problems (as lack of selectivity, drift), which motivate active research in material science, different measurement strategies and signal processing algorithms. Different measurement strategies include sensors arrays, static and dynamic measurements. Several attempts have been focused on dynamic measurements including temperature transient or pulsed techniques and temperature modulation through oscillation of heater voltage, because dynamic measurements of the tin oxide sensor have been suggested that which can provide more information from a single sensor than static measurements do[1-21]. In general, the information obtained from static measurement of chemical sensors is one - dimension , for

基金项目:安徽省自然科学基金《SnO_2 传感器动态检测农药残留的研究》项目资助(010141404)

收稿日期:2007-08-04 **修改日期**:2007-11-21

example, the change in the resistance of a semiconductor gas sensor (ΔR) or response and recovery time. However, these studies always focused on 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. There were a few detailed reports on the essential factor of the dynamic measurement combined with different factors influencing dynamic responses. In our previous work, it was reported rapid detection of pesticide residues using temperature modulation using only a single sensor. It was also reported that the amplitudes of the higher harmonics by FFT exhibited characteristic changes that depended not only on the chemical family of the pesticide gases but also on the concentration of pesticide gases as determined by the dynamic responses of the analysis[22,24].

In this paper, our attention was focused the advantages of oscillating measurements, and the factors influencing oscillating behavior, such as applied potential, duty ratio and applied potential waveform (rectangular, saw-tooth, pulse, sinusoidal, etc.) were discussed throughout the experimental trails. Finally, organophosphorus pesticide residues such as parathion was determined by measuring its oscillating behavior.

1 Experimental

A sol was prepared using a solution of $SnCl_2$, $SbCl_3$, $CaCl_2$ and $SrCl_2$ mixed in ethanol. The amounts of Sb, Ca and Sr were fixed to a ratio of 2.5 mol% M/Sn (M = Sb, Ca, Sr). As a binder, a given amount of commercial glass powder was added to the doped SnO_2 powder formed by calcinating the powder at 500 ℃ for 0.5 h 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. The thick films were sintered at various temperatures for 30 min in air to obtain doped SnO_2 thick films gas sensors. These elements were aged at the working temperature until obtaining reproducible, steady state resistances.

Butanone, acetone, ethanol, methanol, formaldehyde and cyclohexanone were used for probing of oscillating behavior (Sigma-Aldrich). The used device was described elsewhere[22]. A given sample gases were injected into testing chamber. Data acquisition started at the time that after about for 80 s the diffusion of injection gases had reached homegenrous mixture under stirring. The sampling rate was set at two points per second, and it took several minutes to complete measurements.

2 Results and discussion

(1) Static behavior of tin oxide gas sensor

To better study the oscillating behavior of tin oxide gas sensor, its static behavior of butanone, acetone, ethanol, methanol and formaldehyde at a given temperature was firstly studied. The resistance of the sensing element obviously changes upon exposure to the organic gas was found; meanwhile, the response time can be observed from the trend of the static curves. It is also necessary to point out, however, in addition to the changes in resistance and response time there is no other information about reaction processes, so it is difficult to analyze the sensing mechanism of the sampling. For static measurements, only the resistance changes of the sensing element in the initial and final states are observed; no other information can be obtained during the reaction processes.

(2) Oscillating behavior of tin oxide gas sensor

Figure 1 illustrates the oscillating behavior of 0.5×10^{-6} ethanol, methanol, formaldehyde and cyclohexanone of a single tin oxide gas sensor. Experimental conditions were as follows: applied potential, 7 V; duty ratio, 30 s/50 s; rectangular potential mode. Duty ratio is defined: $RA = t_h/(t_h + t_l)$, where t_h and t_l are the time of high level and low level, respectively. As can be seen from Fig. 1, there is sufficient information in the oscillating behavior to identify the sample gases easily. In the four selected species, there are three different functional groups —the hydroxyl group, the aldehyde group and a cyclic ketone; one can easily observe distinguishing features and their connections among the samples by comparing the static behavior. For ethanol and methanol, the oscillating behavior have similar tendencies due to their identical functional group, the hydroxyl group. This case can be explained by taking account of the role of adsorbed oxygen species. During static measurements, adsorbed oxygen oxidizes sample gases on the surface, and chemisorbed oxygen concentration decreases, inducing an increase in conductance. Gas identification in a rectangular temperature modulated mode is related to the different reaction kinetics of the interacting gases on the tin oxide surface. It is clear that, by oscillating method, it is possible to provide surface oxygen species

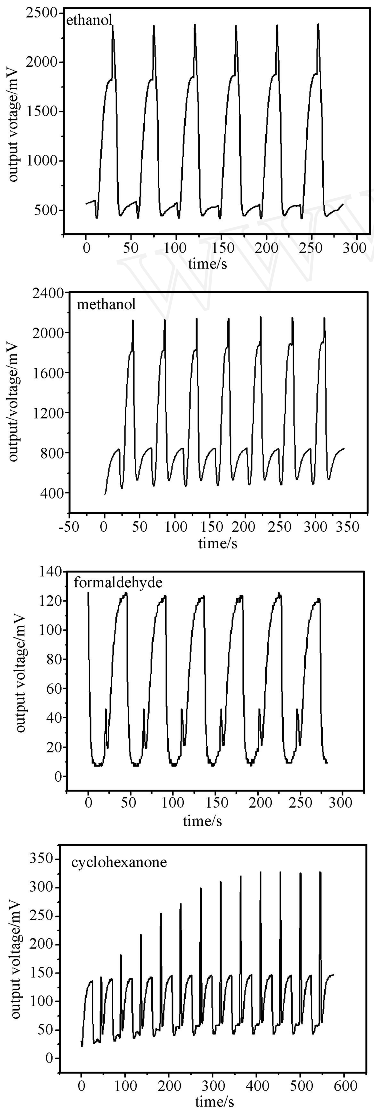

Fig. 1　Oscillating behavior of tin oxide gas sensor to ethanol, methanol, formaldehyde and cyclohexanone. Experimental conditions: sample concentration, 0.5 ppm; applied potential, 7 V; duty ratio, 30 s/50 s; rectangular potential mode.

at constant temperatures, at which under equilibrium conditions, they do not exist. In this way, the reaction with the reducing and oxidizing gases is dramatically influenced, e.g. at lower temperatures and at higher temperatures, the responses to sample gases exhibit their characteristic wave shape due to the reaction with different oxygen species. From these observations, we suggest that the oscillating method is beneficial to analyze the mechanism of detection of the sample gases.

(3) Effect of applied potential at duty ratio of 30 s/50 s

To optimize the selectivity of oscillating behavior of a gas sensor, it is necessary to know a relationship between a given potential and its conductance in the presence of a specific gas. Fig. 2

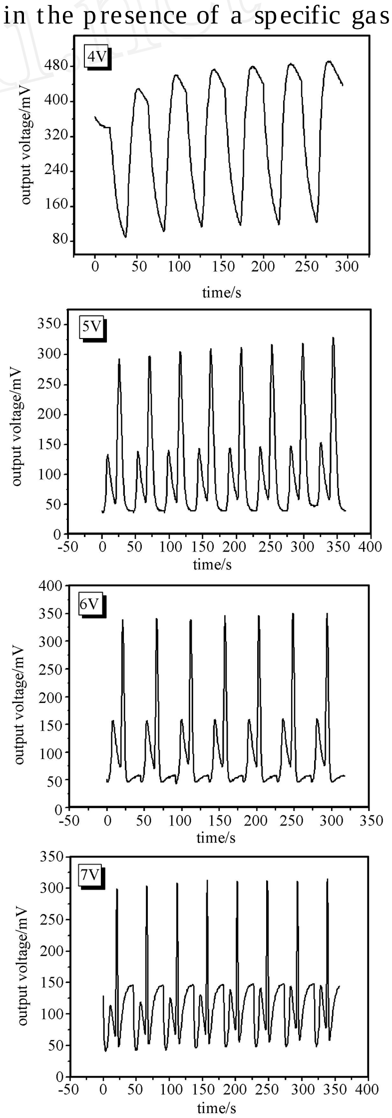

Fig. 2　Effect of applied potential on the responses to 0.5 ppm acetone at a duty ratio of 30 s/50 s in a rectangular mode.

reports the effect of a given potential on the response of 0.5 $\times 10^{-6}$ (ie ppm) acetone at a constant duty ratio of 30 s/50 s in a rectangular mode. As seen in the figure, the different responses at different operating potential are easily observed. In this case the sensor exhibits enhanced selectivity to acetone as potential increases. It suggests that acetone can be identified by a relatively complete response at potential of 7 V. Obviously, there are different surface reaction mechanisms between acetone and chemisorbed oxygen at different given operating potentials.

(4) Effect of duty ratio at an applied potential of 7 V

Fig. 3 clearly shows the time-dependent shape change of the resistance of the sensor in the presence of butanone in air at different duty ratios by controlling the applied potential of 7 V in a rectangular mode. As seen in the figure, one can easily observe the different oscillating behaviors of butanone by applying different duty ratios. When keeping the time of high or low level and changing the time of low or high level, the responses change consequently. Therefore, the duty ratio is important for investigating the oscillating behavior of tin oxide gas sensor.

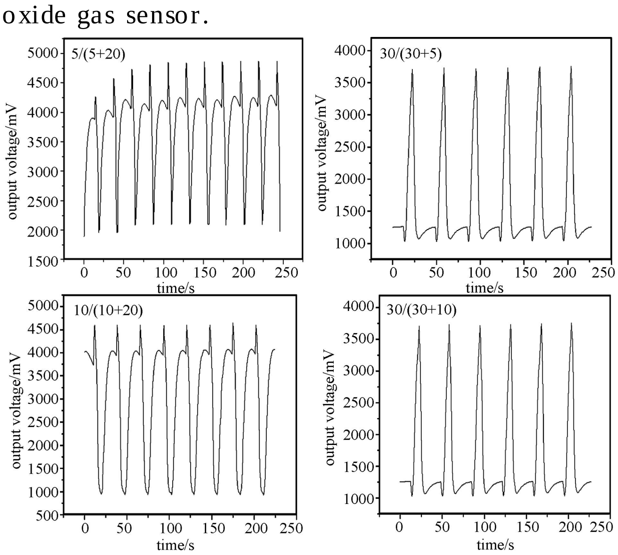

Fig. 3 Effect of duty ratio on the oscillating behavior of ethanol at an applied potential of 7 V in a rectangular mode.

(5) Effect of applied potential waveform

The oscillating behaviors of methanol are shown in Fig. 4 under different applied potential waveforms. Although the sample is the same, we can see that the oscillating behavior are different. These experimental data were in agreement with Ortega's report. Ortega and coworkers have reported that CO and CH_4 can be detected using pulse and triangular heating waveforms[19]. Based on the analysis above, it is concluded that the change of applied potential waveform influences the oscillating behavior of sample gas by changing the surface temperature of the sensing element.

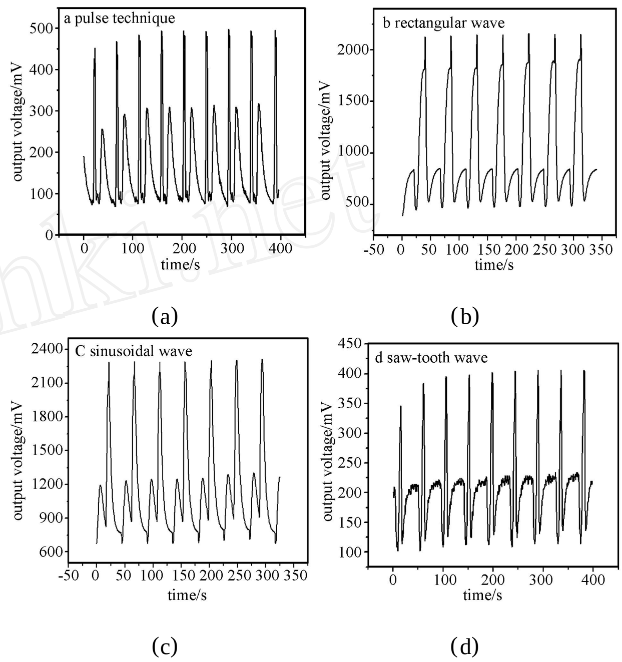

Fig. 4 Effect of applied potential waveform on the oscillating behavior of methanol. Experimental conditions: applied potential 7 V, duty ratio 30 s/(30 + 20) s (a) pulse technique, (b) rectangular wave, (c) sinusoidal wave, and (d) saw-tooth wave.

(6) Detection of parathion under oscillating measurement method

The oscillating behavior of parathion pesticide is presented in Fig. 5. As seen in Fig. 5, it is evident that the oscillating behavior of parathion pesticide differs from that of other organic gases, and it suggests that a good sensitivity and selectivity to pesticide and a sufficient qualitative analysis are achieved.

3 Conclusions

This study have demonstrated the influential factors (i. e., applied potential, duty ratio, and applied potential waveform (rectangular, sawtooth, pulse, sinusoidal)) of the oscillating behav-

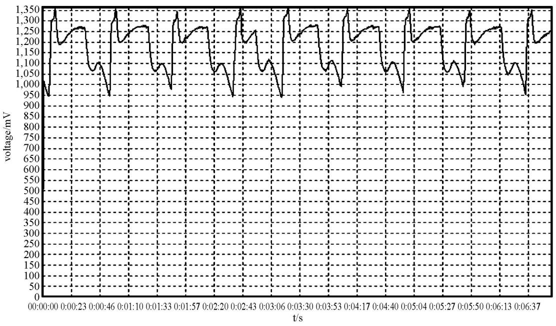

Fig. 5　The oscillating behavior of parathion. Experimental conditions: sample concentration, 0.5 $\times 10^{-6}$; applied potential, 7 V; duty ratio, 30 s/50 s; rectangular temperature mode.

ior of a gas sensor. The characteristic optimum oxidation potential was 7V at a duty ratio of 30s/50s. Experimental data also show that parathion can be detected easily by using this oscillating measurement method.

Acknowledgement

We thank Dr. Huang Xingjiu (University of Science and Technology of China) for his helpful discussion. This work was supported by Anhui Province Natural Science Foundation "Determination study of oscillating behavior of pesticide residues by tin oxide gas sensor" (01041404).

参考文献:

[1] Hiranaka Y, Abe T and Murata H: Sensors and Actuators B [J]. 9 (1992) 177.
[2] Amamoto T, Yamaguchi T, Matsuura Y: Sensors and Actuators B[J]. 13-14 (1993) 587.
[3] Kelleter J, Kohi C-D and Petig H: US Pat. 5668304[P]. September, 16 (1997).
[4] Aigner R, Auerbach F, Huber P: Sensors and Actuators B [J]. 18-19 (1994) 143.
[5] Nakata S and Nakamura H: Sensors and Actuators B[J]. 8 (1992) 187.
[6] Nakata S, Kaneda Y, Nakamura H: Chem. Lett[J]. (1991) 1505.
[7] Romppainen P, Lantto V and Leppavuori S: Sensors and Actuators B[J]. 1(1990) 73.
[8] Lantto V and Romppainen P: J. Electrochem. Soc[J]. 135 (1988) 2550.
[9] Kato Y, Yoshikawa K and Kitora M: Sensors and Actuators B [J]. 40 (1997) 33.
[10] Choi N-J, Shim Ch-H, Song K-D: Sensors and Actuators B [J]. 86 (2002) 251.
[11] Roth M, Hartinger R, Faul R, Sensors and Actuators B[J]. 35-36 (1996) 358-362.
[12] Lee A P and Reedy B J, Sensors and Actuators B[J]. 60 (1999) 35.
[13] Nakata S, Ozaki E and Ojima N: Analytica Chimica Acta[J]. 361 (1998) 93.
[14] Nakata S, Nakasuji M, Ojima N, Applied Surface Science [J]. 135 (1998) 285.
[15] Fort A, Gregorkiewitz M, Machetti N: Thin Solid Films[J]. 418 (2002) 2.
[16] Aigner R, Dietl M, Katterloher R: Sensors and Actuators B [J]. 33 (1996) 151-155.
[17] Heilig A, Barsan N, Weimar U: Sensors and Actuators B [J]. 43 (1997) 45.
[18] Cavicchi R E, Suehle J S, Kreider K G: Sensors and Actuators B[J]. 33 (1996) 142.
[19] Ortega A, Marco S, Perera A: Sensors and Actuators B[J]. 78 (2001) 32.
[20] Ionescu R, Llobet E: Sensors and Actuators B[J]. 81 (2002) 289.
[21] Nakata S and Ojima N: Sensors and Actuators B[J]. 56 (1999) 79.
[22] Huang X-J, Liu J-H, Shao D-L: Sensors and Actuators B [J]. 96 (2003) 630.
[23] Huang X-J, Wang L-Ch, Sun Y-F: Sensors and Actuators B[J]. 99 (2004) 330.
[24] Huang X-J, Liu J-H, Pi Z-X: Talanta[J]. 64 (2004) 538.

刘铁兵(1959-) ,男 ,1982 年 7 月安徽大学分析化学专业毕业 ,研究生、高级工程师 ,参加工作以来主要从事食品、农产品的质量检验和品质研究及质量监督检验的技术业务管理工作 ;2001 年开始重点从事农产品质量监督检验和农业标准化的研究 ,农产品的质量安 全认证工作。先后参加和主持了省部级项目 8 项、专利 3 项、在各类期刊上发表学术论文 12 篇 ,tiebingliu @163. com