A New Method for Detecting Pesticide Residue by Using a Single SnO_2-based Gas Sensor

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Abstract: A new rapid detecting method (called dynamic measurements) to detect and distinguish the presence of two pesticide gases in the atmosphere was reported. The method employed only a single SnO_2-based gas sensor in a rectangular temperature wave mode to perform the qualitative analysis of a binary gas mixture (acephate and trichlorphon) in air. Experimental results show that high selectivity of the sensor achieved in the range of 250 ~ 300℃ and modulating frequency 20 MHz, one can easily observe the qualitative difference among the responses to the pure acephate and trichlorphon of the same concentration and to there mixture.

Key words: SnO_2 gas sensor; dynamic measurements; pesticide residue

一种利用单个 SnO_2 气体传感器检测农药残留的新方法

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摘要：研究了一种在环境气氛中快速检测和识别农药残留(敌百虫和乙酰甲胺磷)的新方法，即动态检测方法。这种方法是利用单个 SnO_2 气体传感器在方波变化的温度下完成对敌百虫和乙酰甲胺磷及其混合气体的定性分析。实验结果表明，SnO_2 气体传感器在温度范围为 250 ~ 300℃、温度变化频率为 20 MHz 的工作条件下对敌百虫和乙酰甲胺磷及其混合气体表现出高的灵敏度和清晰的动态特征响应。

关键词：SnO_2 气体传感器；动态检测；农药残留

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SnO_2-based gas sensors have been extensively applied to gases detection[1]. Their magnificent advantages are low cost and high sensitivity; but disadvantages such as instability and selectivity also exist[2,3]. In practical applications, several attempts have been made to overcome the shortcomings through, for example, separating the components with chromatographic columns, operating at different temperatures, and choosing different burning-in procedures, dopants, surface chemical modification, measuring frequencies, etc[1-6]. For common applications of

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pattern recognition and multi-component analysis of gas mixtures, arrays of sensors[7,8] were usually chosen and operated at constant temperature. In these cases a lack of selectivity or overlapping sensitivities among different sensors was of advantage[9,10]. Some authors[11~14] had indicated that temperature modulation of metal-oxide sensors provides more information from a single sensor than isothermal operation, allowing improved research works in gas detection such as CH_4, CO, NO_2. Several investigations have been focused on dynamic sensor measurements obtaining adequate results, and nevertheless they used non - commercial sensors and often required sophisticated heater control waveforms[15,16].

Pesticide residue has always been the most important problem on food security[17,18]. In recent years, therefore, considerable effort has been directed towards the detecting techniques of pesticide residue[17~22]. Although there had precision of analysis, it is well-known that the disadvantages of the conventional detecting method, such as chromatographic detection, is too slow to detect gas sample in situ and affects the timeliness of the analysis. So more attention had been focused on the research of rapid test method of pesticide residue. At present, the rapid analyzing techniques included immunoassay[19], biosensor[20,21], chromatographic and mass spectrometry[22], polarographic method[23] and so on. A simplified indirect method was developed using adapted versions of molecular emission cavity analysis based on measurements of the intensity of the emission band of indium monochloride at 359.9 nm[24], but in the case of the above mentioned methods there exist some different limitations[17]. Meanwhile, there was very few of reports about detecting pesticide residue by using SnO_2 sensor.

In the present study, a modulated temperature operation mode was chosen as a new approach to improve the selectivity of a gas sensor to detect acephate and trichlorphon in the controlled way, and to reduce the overall power consumption by employing only a single sensor rather than an array. These pesticide gases were chosen as they are of practical significance in monitoring poisoning from vegetable, foodstuff, melon and fruit, and so on. The concentration 0.1×10^{-6} was chosen as it represents the maximum residue value according to criterion of Ministry of Health, P.R.China.

1 Experimental

The thick film sensors were made by depositing thick films of tin oxide on ceramics substrates[25]. The voltage values of a known resistance were measured by using a electronic circuit. The measuring electronic circuit can be found in Ref[26]. The preparation of the sensitive material was described elsewhere[27]. The grain sizes of the materials were around 20 nm and 50 nm. The temperature of the sensors was varied between 50℃ and 300℃ by a rectangular modulation of the heating voltage with a frequency of 20, 25, 30 or 50 MHz. The experimental test setup consisted of computer-driven mass flow controllers, a Teflon chamber and a multimeter for measurements in the millisecond range. The temperature was varied by modulating the heating voltage with a power supply (HP 6035A) driven by a frequency generator (HP 3325B). A flow of compressed air was used as purging gas. Test gases were 0.1×10^{-6} acephate and trichlorphon (Analytical standard, provided by Sigma-Aldrich Laborchemikalien GmbH).

The gas response was defined as the ratio R_{air}/R_{gas} between the resistance of the sensor in a clean air and the resistance in a test pesticide gas coexisting air.

2 Results and discussion

2.1 The static response of the sensor to trichlorphon and acephate gas atmosphere

The responses to 0.1×10^{-6} trichlorphon, acephate and their 0.2×10^{-6} mixture gases at 300℃ for SnO_2 sensor are shown in Fig.1. The response time is time taken for the sensor response to reach 90% of the saturation value after the test gas contacts with the surface of the sensor. In Fig.1, one can clearly observe that the sensor exhibits the rapid response upon exposure to the trichlorphon and acephate gas. It is noticed that the response time to both acephate and trichlorphon gas or to 0.2×10^{-6} mixture was only several seconds. It also showed that, however, in addition to the changes in resistance and response time there were no other information about reaction processes. In particular, there was no reaction phenomenon but declining of element resistance by comparing with each pesticide gas, this case can be explained by the fact that

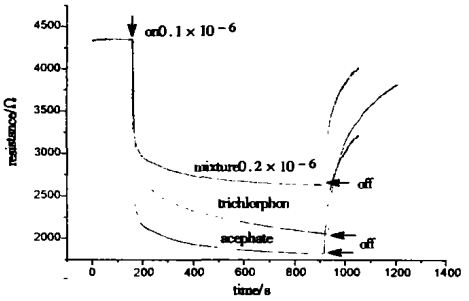

Fig.1 Static response characteristics of the sensor to trichlorphon, acephate and mixture gas atmosphere (operating temperature: 300℃)

the concentration of the mixture was larger than that of the single gas. That is to say, during static measurements, only the resistance changes of the sensing element in initial and final state were observed, in the cases of other changes during the reaction process any information were not obtained.

2.2 The dynamic response of the sensor to trichlorphon and acephate gas and their mixture

Fig.2 shows the typical dependence of the sensor resistances of the sensors on time realized with the 20 MHz modulating frequency, during their exposure to 0.1×10^{-6} trichlorphon gas, 0.1×10^{-6} acephate gas and mixtures. Comparing these response wave shapes with that in air, one can easily observe the qualitative difference among the responses to pure gases of the same concentration and to the mixture. One can also observe a huge sensitization to the pesticide gases. This effect can be explained by taking into account the characteristics of SnO_2 with sensing material and O_2 adsorption on the surface of SnO_2 under a temperature modulated mode.

It is widely accepted that oxygen in air is chemisorbed and decomposed as O_2^-, O^- and O^{2-}. At a constant temperature, there exists a equilibrium state at the surface of 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 gas phase. The reaction steps involved the low – temperature surface reactions and the high-temperature bulk reactions between point defects in the SnO_2

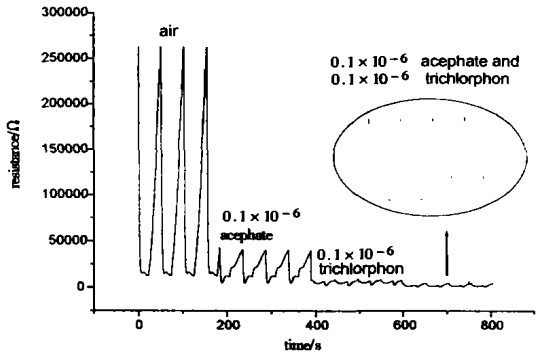

Fig.2 Time-dependence changes of the resistance during the temperature modulation (20 MHz) in (1) air, (2) 0.1×10^{-6} trichlorphon gas, (3) 0.1×10^{-6} acephate gas, (4) mixture gas of 0.1×10^{-6} trichlorphon and 0.1×10^{-6} acephate

crystal and oxygen (O_2) in gas phase. The first step is composed of adsorption and catalytic reactions at active sites (the latter involving intrinsic point defects, such as oxygen vacancies, and/or extrinsic point defects, such as 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 involve adsorbed negatively charged molecular(O^{2-}) or atomic(O^-) oxygen species as well as hydroxyl groups (OH) at different surface sites.

During the static measurement process, the adsorbed oxygen results in oxidation of pesticide gases on the surface and in a decrease of chemisorbed oxygen concentration, inducing an increase of the conductance. As seen from Fig.2, it is found that gas identification in a rectangular temperature modulated mode is related to the different reaction kinetics of the interacting gases on the tin oxide surface. Although the detailed reaction mechanism of pesticide gases is not clear, but here it may be known by temperature modulation to provide that there exist no surface oxygen species in equilibrium condition at constant temperature. In this way the reaction with the reducing and oxidizing gases was dramatically influenced, e.g. at lower temperatures and at higher temperatures the response to pesticide gases acephate and trichlorphon exhibited their characteristic wave shape due to the reaction with different oxygen species. Comparing the results with section 2.1,

for constant temperature measurements one can not observe the characteristic wave shape of the pesticide gases.

2.3 Effect of temperature on gas response of the sensor

Fig.3 shows a plot of the gas response of the sensor as a function of a constant concentration of acephate, trichlorphon and mixture gas at different operation temperatures. It was evident that the sensor exhibited a significant increase in the sensitivity upon exposure to a very low concentration of acephate, trichlorphon and mixture gas, at round 300℃ the sensitivity reached maximum, then decreased with the increase in operation temperature subsequently.

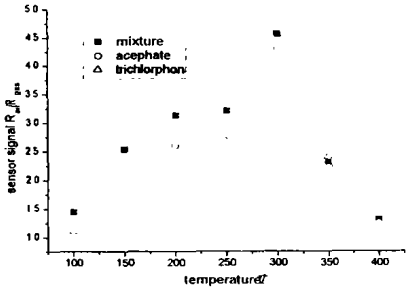

Fig.3 The gas response(defined as the ratio R_{air}/R_{gas}) as a function of 0.1×10^{-6} trichlorphon, acephate gas and 0.2×10^{-6} mixture respectively at different temperature

2.4 Effect of temperature modulating frequency on the response of test gas

Figs. 4 and 5 clearly show the time-dependence change shape of resistance of the sensor in the presence of trichlorphon and acephate gas in air under different temperature modulating frequency by controlling temperature range of 250 ~ 300℃. Obviously, temperature modulating frequency had a significant effect on the sensing behaviour of the sensor. With the decrease in modulating frequency the sensing characteristics of the sensor was clearly different to whether acephate or trichlorphon gas. Meanwhile, other experimental results (frequency < 20 MHz) showed that there were no changes of sensing characteristics.

2.5 Effect of temperature under constant frequency 20 MHz

To optimize the selectivity of a temperature modulated sensor, it was necessary to obtain a relationship between given temperature and its conductance response in the presence of specific gas. Fig.6 shows the effect of

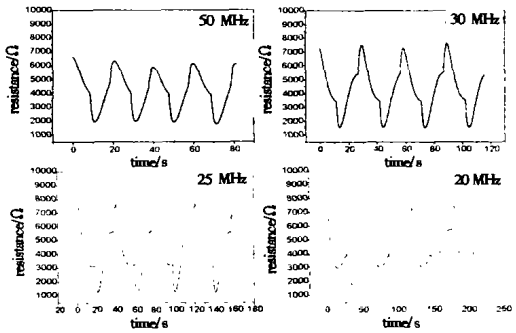

Fig.4 Effect of modulated temperature frequency on the response of 0.1×10^{-6} trichlorphon

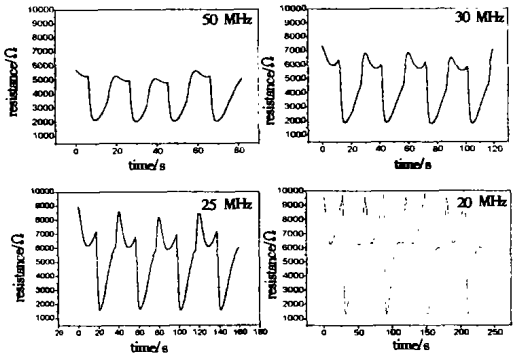

Fig.5 Effect of modulated temperature frequency on the response of 0.1×10^{-6} acephate

temperature on the response of pesticide residue gas, for example, 0.1×10^{-6} trichlorphon under a constant modulating frequency 20 MHz. From this figure, one can easily observe the evidently different signal in different temperature ranges. This case noted that the sensor exhibited enhanced selectivity to trichlorphon gas with temperature increasing. Combining with section 2.4, it is suggested that the trichlorphon gas is identified by means of a relatively complete response signal in the temperature modulating range of 250 ~ 300℃. As the sensor cooled, it was found that the resistance not only increased but also decreased; and, upon heating, the resistance not only decreased but also increased. Obviously, there are different surface reaction mechanisms between trichlorphon and chemisorbed oxygen under different temperature ranges.

Finally, it is necessary to note that different heating shape waveforms such as pulse, sinusoidal, triangular, and saw-tooth, etc. have been used in order to facilitate the feature extraction of the most significant output signal so that the pesticide residue gases can be identified.

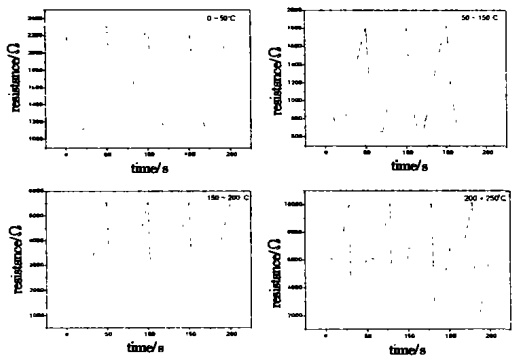

Fig.6 Effect of temperature on the response of 0.1×10^{-6} trichlorphon gas under frequency 20 MHz

Meanwhile, two methods of data analysis have been used - a qualitative one using polar plots and a quantitative one using neural networks. Herein, the feature extraction has been performed by FFT [28].

3 Conclusion

The present experiments revealed that very low concentration pesticide gases (acephate and trichlorphon 0.1×10^{-6}, respectively) in the ambient atmosphere were rapidly detected and distinguished clearly by use of only a single SnO_2 sensor operated in the rectangular temperature mode. The optimizing temperature was between 250 and 300℃ and the optimizing modulating frequency was 20 MHz. It is considered that it will become a significant and exploratory development method to rapidly detect pesticide residue gas. Additional studies are now on the way to extend this approach to identify other pesticide residue gas mixtures with more components and to understand the basic physical phenomena. Future work will also be devoted to the development of appropriate feature extraction procedures for this non-linear frequency-time problem.

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3 结束语

数字滤波器与模拟滤波器都具有改变输入信号所含频率分量的作用,不同的是实现方式不同。数字滤波的数值运算方式使其应用更加简单易行,并可以获得很高的性能指标,运算量小,具有高精度,高稳定性的特点,可实现温度实时控制。

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