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Zinc oxide thin-film chemical sensors in conjunction with neural network pattern recognition for trimethylamine and dimethylamine gases

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Transient response curves for exposure to several gases are observed using zinc oxide (ZnO) thin-film gas sensors. It is found that an aluminium-doped ZnO (ZnO:Al) sensor exhibits a high sensitivity and an excellent selectivity for amine gases. In order to discriminate between gas species such as trimethylamine (TMA), dimethylamine (DMA) and other gases, pattern recognition analysis using a neural network is carried out using parameters which characterize the transient responses of the sensor for exposure to gases. The recognition probability of the neural network is 90% for TMA and DMA with constant concentration and is 100% for TMA and DMA with different concentrations, except for a concentration of 1 p.p.m.

1. Introduction

It is known that the use of gas sensor arrays in conjunction with an associated pattern recognition analysis yields advantages for identification of gases [1–4]. In pattern recognition analysis using the sensitivity change of each sensor for various gases as the sensor output, the recognition probability is, however, affected by the sensitivity fluctuations of the sensors. The success of this approach thus depends upon the choice of parametric expression used to define the array output. The objective of this work is to demonstrate a novel gas sensing system using zinc oxide (ZnO) thin-film gas sensors in conjunction with a neural network pattern recognition method, which is useful for discriminating between trimethylamine (TMA), dimethylamine (DMA) and other gases.

2. Experimental procedure

Non-doped ZnO and aluminium-doped ZnO (ZnO:Al) thin films were prepared on Corning 7059 glass substrate using magnetron sputtering. In the preparation of non-doped ZnO thin film, ZnO powder with a purity of 99.9% was used as a target. In the preparation of ZnO:Al thin films, a powder mixture of ZnO and dopant aluminium oxide (1–5 wt % Al_2O_3) was used as a target. Sputtering deposition was carried out at a pressure of 0.2–0.8 Pa in pure argon gas with a power of about 50–80 W. A pair of parallel gold electrodes was evaporated on to the ZnO:Al thin film in a vacuum. Details of the sputtering system have been described elsewhere [5–8].

The sensing characteristics of the ZnO:Al thin-film gas sensor, which was set on a heater in a glass bell-jar as schematically shown in Fig. 1, were observed by measuring the resistance change of the sensor when the sensor operated in ambient air was exposed to testing gases such as TMA, DMA, acetone (CH_3COCH_3), methanol (CH_3OH), ethanol (C_2H_5OH), hydrogen (H_2) and carbon monoxide (CO). The operating temperature (T_{op}) of the sensor was about 450 °C. The resistance change R_a/R_g of the sensor was calculated from the output voltage change across a load resistance connected in series with the sensor under an applied d.c. voltage of 1 V, where R_a is the resistance of the sensor at the operating temperature in air and R_g after exposure to the testing gas.

3. Results and discussion

Figs 2, 3 and 4 show typical transient response curves of non-doped ZnO, ZnO:Al (2.5 wt %) and ZnO:Al (5.0 wt %) thin film gas sensors, respectively, for exposure to various gases. It should be noted that the sensors exhibit a large resistance change for exposure to TMA and DMA and the sensitivity strongly depends upon the content of Al impurity doped into ZnO thin film. The most noticeable result is the shape of the transient response curves for TMA and DMA, which are characterized by a decrease in R_a/R_g with transit time after saturation, although R_a/R_g for exposure to other gases remained saturated with increasing transit time. It was confirmed that the sensor response for TMA and DMA was not affected by H_2O and/or CO_2 in the ambient air. These results suggest that ZnO sensors, especially the Al-doped ones, have a high sensitivity and an excellent selectivity for TMA

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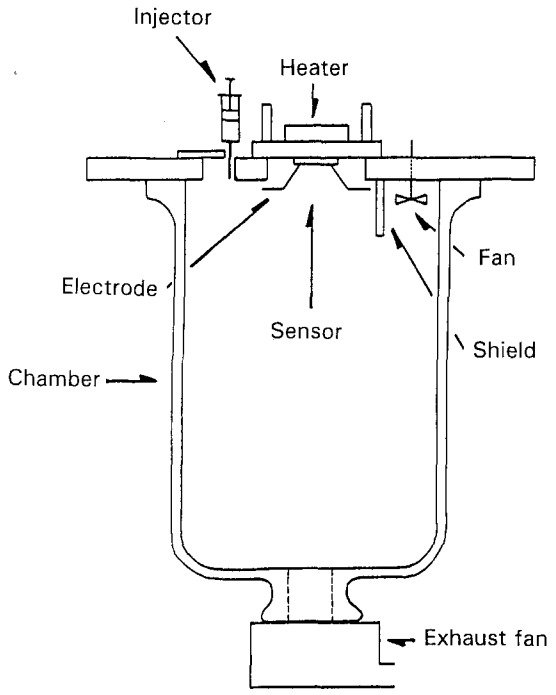

Figure 1 Schematic diagram of the sensing chamber.

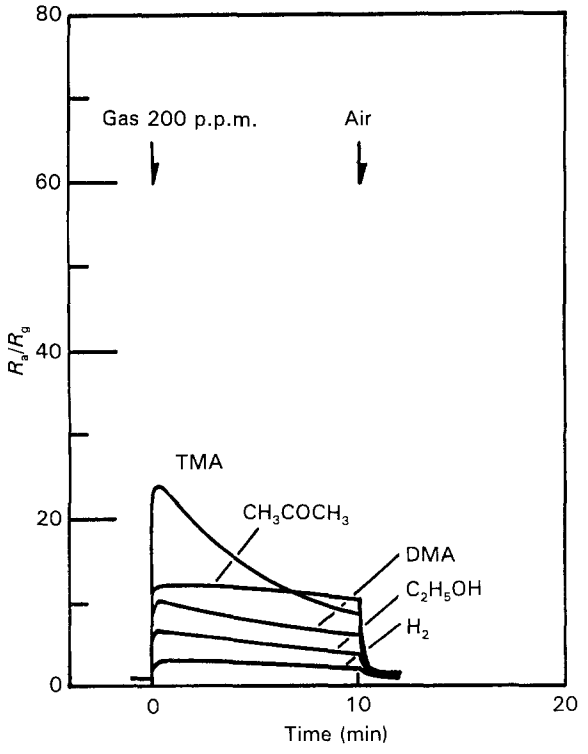

Figure 2 Transient response curves of non-doped ZnO thin-film gas sensor for exposure to various gases (200 p.p.m.).

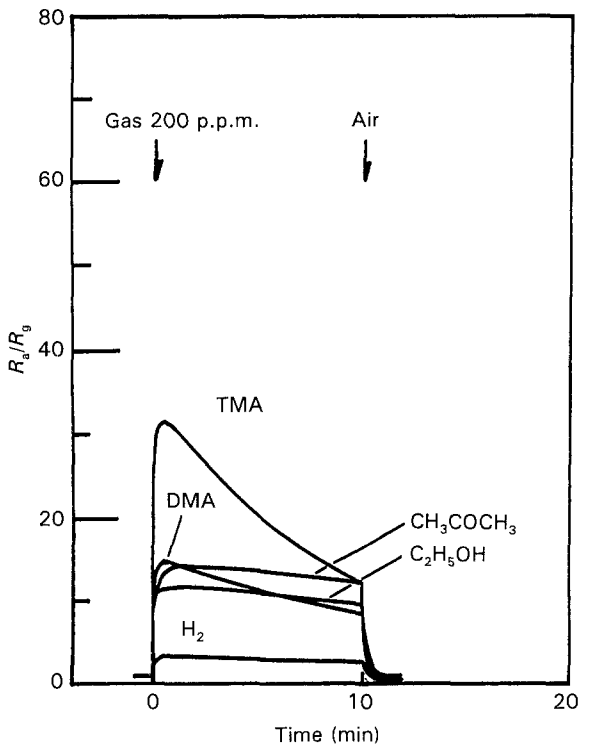

Figure 3 Transient response curves of ZnO:Al (2.5 wt %) thin-film gas sensor for exposure to various gases (200 p.p.m.).

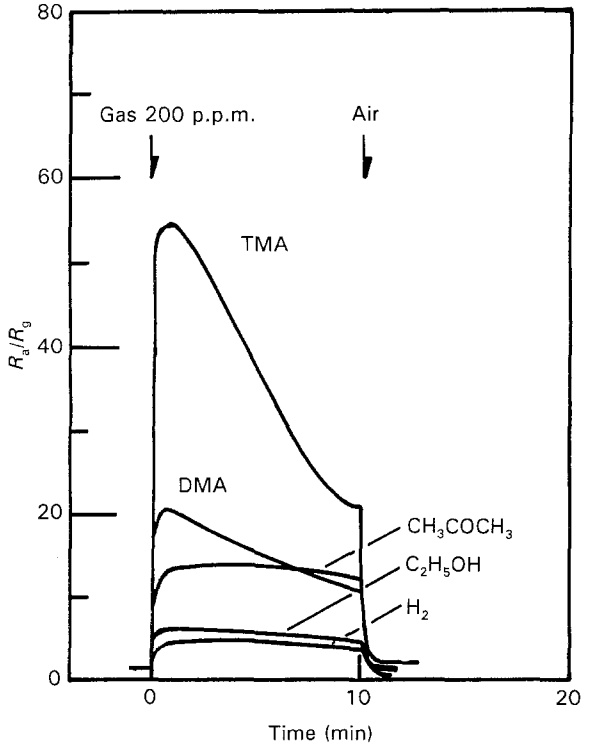

Figure 4 Transient response curves of the ZnO:Al (5 wt %) thin-film gas sensor for exposure to various gases (200 p.p.m.).

and DMA. It was confirmed that the sensors have a high sensitivity even for exposure to TMA with a concentration of 1 p.p.m. [6, 7].

In order to discriminate gas species such as TMA, DMA and other gases, using principal component analysis [2, 9, 10] or neural network pattern recognition analysis [1, 9], we defined three parameters such as S_{max} (maximum resistance change), T_{max} (time at maximum resistance change), S_{10}/S_{max} (ratio of S_{max} to resistance change S_{10} after 10 min from onset of transient response), as shown in Fig. 5. The pattern recognition analysis was carried out for the transient response curves of ZnO:Al (2.5 wt %) and ZnO:Al (5.0 wt %) sensors for exposure to gases with a constant concentration of 200 p.p.m. The results of principal component analysis, reduced to the first two principal components for the visualization of multi-dimensional data, are given in Figs 6 and 7, respectively. As

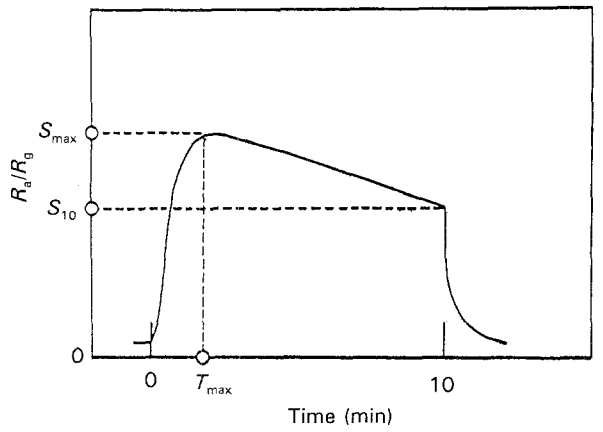

Figure 5 Typical transient response curve of a sensor, showing the three parameters S_{max} (maximum resistance change), T_{max} (time at maximum resistance change) and S_{10}/S_{max} (ratio of S_{max} to resistance change S_{10} after 10 min from the onset of transient response).

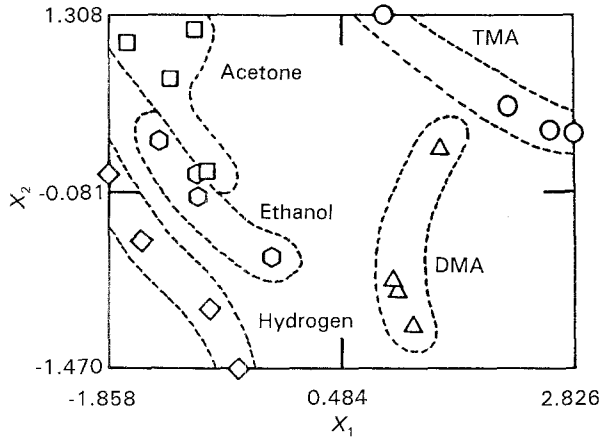

Figure 6 Principal component plot (X_1, against X_2) from results for TMA, DMA and other gases, observed using ZnO:Al (2.5 wt %) thin-film gas sensor.

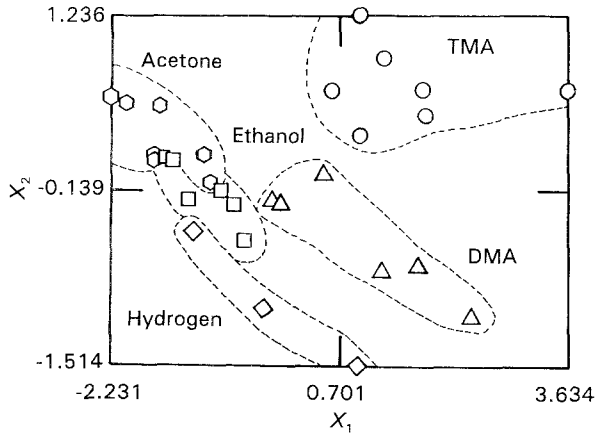

Figure 7 Principal component plot (X_1 against X_2) from results for TMA, DMA and other gases, observed using ZnO:Al (5 wt %) thin-film gas sensor.

can be seen, there is a good separation between TMA, DMA and other gases for each case, though the cluster boundaries for acetone, ethanol and hydrogen are not clear. These results suggest that it is possible to discriminate between TMA, DMA and other gases using neural network analysis.

The neural network used had a three-layer structure made up of three input, three hidden and three output units as shown in Fig. 8. After each neuron unit collects the sum of weighted inputs from the first layer, its output is determined by putting the sum into a non-linear function. The network was initially trained 5000 times using data so as to obtain the desired output when a certain pattern was fed from the sensor. The back-propagation algorithm proposed by Rumelhart *et al.* [11] was applied as the learning rule. The recognition probability was defined as the ratio of the number of right answers to that of the total trials. Consequently, the recognition probability of the neural network analysis for data from transient response curves observed using ZnO:Al (2.5 wt%) or ZnO:Al (5 wt %) sensors was 90% for 15 or 30 trials, respectively, as listed in Tables I and II. Although the recognition probabilities listed there are fairly high, these are for the cases using constant amounts of the testing gases. In most practical cases, the concentration of gases is, however, not constant, so it is necessary to be able to identify each gas when the concentration of testing gases is not constant.

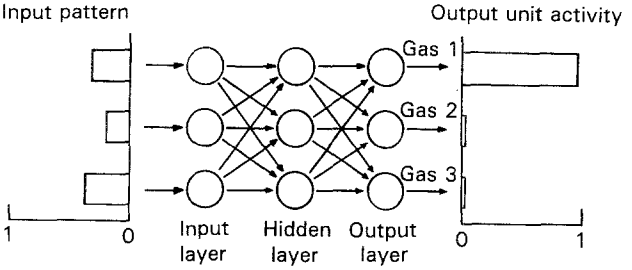

Figure 8 Schematic diagram of the structure of a neural network consisting of three input, three hidden and three output layers.

TABLE I Identification results of neural network analysis for gases with a constant concentration of 200 p.p.m. using ZnO:Al (2.5 wt %) and ZnO:Al (5.0 wt %) thin-film gas sensors

Sample	Identification		
	TMA	DMA	Others
TMA	2	1	0
DMA	1	2	0
Acetone	0	0	3
Ethanol	0	0	3
Hydrogen	0	0	3

TABLE II Identification results of neural network analysis for gases with a constant concentration of 200 p.p.m. using ZnO:Al (5 wt %) thin film gas sensor

Sample	Identification		
	TMA	DMA	Others
TMA	5	1	0
DMA	1	5	0
Acetone	0	0	6
Ethanol	0	1	5
Hydrogen	0	0	6

TABLE III Identification results of neural network analysis for gases with different concentrations using non-doped ZnO ZnO:Al (2.5 wt %) and ZnO:Al (5.0 wt %) thin-film gas sensors

Sample	Concentration (p.p.m.)	Identification		
		TMA	DMA	Others
TMA	1	×	×	○
	10	○	×	×
	100	○	×	×
	1000	○	×	×
DMA	1	○	×	×
	10	×	○	×
	100	×	○	×
	1000	×	○	×

First of all, we tried to discriminate between gases using parameters which are the same as those in the cases of constant concentration, but we could not discriminate successfully. An experiment to discriminate TMA and DMA gases with different concentrations was therefore carried out using three kinds of ZnO sensor in conjunction with neural network analysis. The parameter used in this case was S_{10}/S_{max}, obtained from the transient response curves of non-doped ZnO, ZnO:Al (2.5 wt %) and ZnO:Al (5 wt%). The results of neural network analysis for gases with different concentrations are listed in Table III. In all cases except for 1 p.p.m., the discrimination probability between TMA and DMA was 100% although only six trials were carried out. This result suggests that it is possible to discriminate between TMA and DMA gases with different concentrations by using appropriate sensors and parameters for neural network analysis.

4. Conclusions

Discrimination between TMA, DMA and other gases was successfully demonstrated using ZnO:Al thin film gas sensors in conjunction with neural network pattern recognition. The new feature of this method is to use parameters which characterize the transient response curves. The novel sensing system demonstrated here is one of the most attractive candidates for gas discrimination, since the sensing system is so simple. Studies on the sensing mechanism of the Al-doped ZnO thin film gas sensor for TMA and DMA is now in progress.

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