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RESEARCH ARTICLE

STATISTICAL ANALYSES OF CONDUCTANCE TRANSIENTS TO DISCRIMINATE THE GAS TYPE

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ABSTRACT

In the present work various toxic and combustible gases such as CO and CH_4 could be well discriminated using ZnO thin film gas sensors from statistical analysis of their conductance transients. ZnO thin films are grown using MOCVD technique. The gas sensing characteristics of the grown films are studied at different operating temperatures in presence of various gases. The first Fourier transformation (FFT) yield excellent results in discriminating the gases at different operating temperatures.

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INTRODUCTION

ZnO is an II-IV semiconducting metal oxide which is well explored in various sectors. Numerous applications of this material particularly in its thin form is studied widely which includes, transparent conductors (Minami, 2000), solar cell (Nuruddin, and Abelson, 2001), Varistors (Brankovic *et al*., 2000), gas sensors (Shewale *et al*., 2013), etc. There are various literature reports showing excellent gas sensing characteristics of these ZnO thin film gas sensors in detecting different toxic and combustible gases (Pati *et al*., 2014; Bai *et al*., 2013). Although the sensing applications of ZnO are extensively studied, still the lack of selectivity hinders its use in various applications. This selectivity study is also reported in the literature (Pati, 2015). However, the success of this study still remains a challenge particularly for thin film type sensing elements. In this work, ZnO thin films were deposited by MOCVD growth technique. The gas sensing characteristics are investigated in presence of CO and CH_4 at different operating temperatures. Statistical analysis of the conductance transients is used to study the cross selectivity of these sensors. It is said that these sensors can be used in discriminating various gases in a mixed gas environment.

EXPERIMENTAL

In the present study MOCVD growth technique was used to grow ZnO thin films on the fused quartz substrates. Diethyl-zinc and tert butanol were respectively used as the zinc and oxygen precursors and N_2 gas was used as carrier gas. Using a number of mass flow controllers the flow rates of precursors were maintained at their required level. The temperature and pressure of the chamber were maintained at 450 ^oC and at atmospheric pressure respectively. The details of the MOCVD growth procedure was illustrated elsewhere (Pati *et al*., 2014). Gas sensing characteristics of the grown films in presence of hydrogen and carbon dioxide were studied using a dynamic gas sensing unit, the details of which was provided elsewhere (Mukherjee and Majumder, 2009). The conductance transients upon exposure of CO and CH_4 were recorded at various operating temperatures (250 ^oC, 300 ^oC, 350 ^oC and 380 ^oC). The fast Fourier transformation (FFT) was used to extract the required features of the measured conductance transients and taken as the input to statistical analysis (PCA).

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RESULTS AND DISCUSSION

Fig. 1 shows the resistance transients during response and recovery of 500 ppm of (a) CO and (b) CH_4 gases recorded at different operating temperatures such as 250 ^oC, 300 ^oC, 350 ^oC and 380 ^oC.

From these transients the response% is estimated using the relation (Pati *et al.,* 2015)

$$S(\%) = \frac{R_a - R_g}{R_a} \times 100 \tag{1}$$

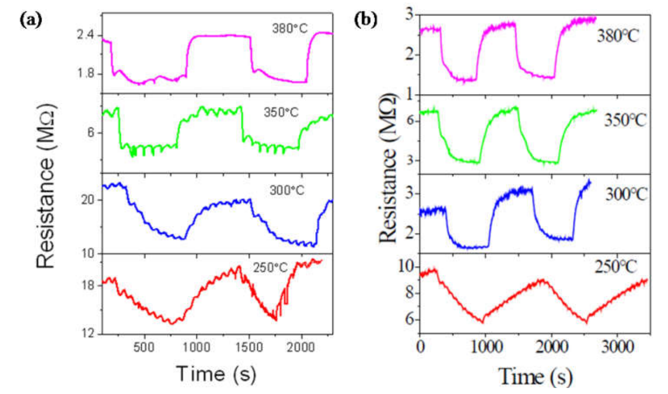

Fig. 1. Temperature dependent resistance transients of ZnO thin film in presence of different gases (a) CO, and (b) CH_4

Where R_a and R_g are the resistance of the sensor in air and test gas environment respectively. Now this response% is plotted in Fig. 2 (a). From the figure it is observed that the sensor can detect well both CO and CH_4 at each operating temperature. Hence, in a mixed gas environment this sensor may not differentiate the individual gas type. Therefore, to study this cross selectivity issue we have recorded a number of conductance transients in presence of CO and CH_4 gas at each operating temperatures. Then each transient is analyzed using FFT.

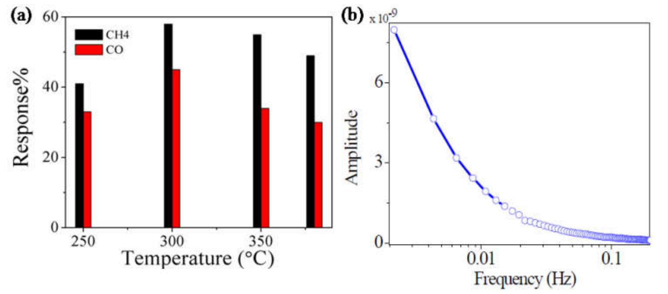

Fig. 2. Shows (a) the temperature variation of response % of the sensor in presence of a fixed concentration (500 ppm) of CO and CH_4 gases, (b) The Fourier spectrum of conductance transient in presence of 500 ppm CH_4

Fig. 2(b) represents one typical Fourier spectrum of conductance transient in presence of 500 ppm of CH_4. For this the large time domain data is converted into frequency domain which is the specific descriptors of each gas at different ppm. For the frequency domain analysis we have done FFT of the whole transient and then extract amplitude of first 10 consecutive low frequency harmonics including dc one. We have repeated each experiment and similarly extract the features by the mentioned technique. The amplitude is estimated from the real and imaginary part of the Fourier coefficients. Thus using the amplitude of first 10 consecutive harmonics we have constructed the data matrix at individual temperatures that is at 250 ^{o}C, 300 ^{o}C, 350 ^{o}C and 380 ^{o}C. Low amplitude harmonics at higher frequencies are affected by noise and are discarded as they do not bear significant information of the particular gas type. The data matrices extracted from FFT analyses are used as input to principal component analysis (PCA).

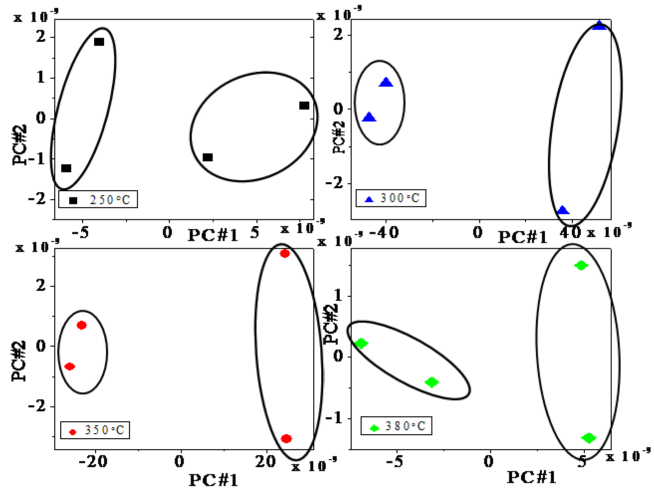

Fig. 3. The plot of principal component 2 (PC#2) versus 1 (PC#1) estimated from the principal component analyses (PCA) for all the transients in presence of 500 ppm of CO and CH_4 at different temperatures

The mathematical details of these analyses can be found elsewhere (Maity *et al*., 2012; Joliffe, 1986). The dimension of the data is reduced by principal component analysis (PCA) into two components like PC#1 and PC#2 which is then plotted against each other, as shown in Fig. 3. As estimated from the figure the maximum class separation of data points is at 300 ^{o}C. The calculated Euclidean distance between two types of gas cluster for FFT PCA was estimated at 8.7, 87.72, 48.67 and 10 at four different temperatures. The maximum class separation is obtained at 300 ^{o}C where the two gases are well separated. It signifies that this analysis can be used to differentiate the gas type in a mixed gas environment.

Conclusion

In this work it is demonstrated that using statistical analysis of the conductance transient one can differentiate a particular gas in a mixed gas environment. Principal Component Analysis (PCA) is used to differentiate the gas types. The data matrices extracted from FFT of the conductance transients (of MOCVD grown ZnO thin film gas sensors) recorded in presence of CO and CH_4 gas are used as input parameters in this analysis. It is said that the FFT PCA combination yield satisfactory results in discriminating the gas types.

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