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Study of Cross Selectivity of Indium Doped Zno Thin film Gas Sensors useing Pattern Recognition Techniques

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Abstract:-Using the low cost sol gel spin coating technique indium doped ZnO thin films are synthesized. Structural and micro structural characteristics of all the grown films are studied using X ray diffraction analysis and field effect scanning electron microscopy respectively. Gas sensing characteristics are studied in presence of various concentrations of H_2, CO and CH_4, at different operating temperatures using a dynamic volume gas sensing measurement unit. Cross selectivity of the sensors towards all the gases is analyzed using pattern recognition technique. From this analysis it is observed that individual gases at each ppm level form well distinct clusters. The observed results demonstrated that PCA using FFT yield promising results in selective detection of the gases.

Keywords- *Indium doping, Gas sensor, Pattern recognition analysis, PCA, FFT*

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1. Introduction

Undoped and doped ZnO thin films exhibit excellent gas sensing characteristics [1-2]. However, their cross selectivity towards these gases restricts their commercial use. In general, the problem of cross selectivity also inhibits to determine the content of a specific gas in a gas mixture. Limited works have so far been reported to study this issue of thin film type gas sensors. For thick film type as well as sintered block type sensing elements the adopted strategies to address the cross selectivity can be categorized into three major categories. First, depending on gas type, the sensor response% has been maximized at different operating temperatures [3-4]. Second, by using catalyst, response% is maximized for a specific gas type [5-6]. Third, noise spectroscopy analyses of conductance transients have been adopted to address the selectivity issue [7]. However, all the mentioned techniques have limited success in thin film type sensors.

In the present work we have adopted feature extraction method of the conductance transients along with pattern recognition algorithms to investigate the cross selectivity of indium doped ZnO thin film gas sensors towards combustible gases (viz. CH_4, CO and H_2). For this, first the conductance transients on exposure to each of the above gases at fixed concentration (~ 1660 ppm), are measured at different operating temperatures. Then the optimum temperature corresponding to the maximum response is noted for the individual gases. Now at the optimum temperature the conductance transients are recorded for various concentrations of each gas. Then using first Fourier transform (FFT) the important features of the conductance transients are extracted. Selected coefficients from FFT analyses are used as input parameter in linear unsupervised (principal component analysis (PCA)) pattern recognition techniques.

2. Experimental

Indium dopes ZnO [$Zn_{1-x}In_xO$ ($0.0 \leq x \leq 0.10$)] thin films were synthesized by sol gel spin coating technique [8]. The structural characteristics of the grown films were studied using X-ray diffractometer (Ultima III, Rigaku, Japan) with Cu Kα radiation. The microstructure of the grown films was investigated by FESEM (SUPRA-40, Carl Zeiss, Germany). To study the gas sensing performance, gold electrodes are deposited on the surface of each of these thin films (sensing elements). For pattern recognition analyses, the gas sensing performance of these sensing elements are evaluated using dynamic flow gas sensing measurement set up described elsewhere [9]. In the dynamic gas sensing unit H_2, CO and CH_4 are used as test gas and commercial air is used as carrier gas. First the optimum operating temperature corresponding to the maximum response for each test gas is estimated. Then at the optimum operating temperature for each of this test gas, a number of response and recovery transients are recorded for various gas concentrations ~ (1660-200 ppm). After necessary data acquisition, the conductance transients are fast Fourier transformed (FFT) using Labview® (Labview-8.5, National Instruments, USA) and MATLAB® (MATLAB 7.8.0.347-R2009a, MathWorks, USA) software. The linear unsupervised pattern recognition analyses (PCA) are performed using commercial statistics analysis software (STATISTICA-9, StatSoft, USA) in conjunction with MATLAB®.

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3. Results and Discussion

3.1. Structural and micro structural characteristics

The structural and micro structural characteristics of the grown films are investigated using X-ray diffraction analysis and field emission scanning electron microscopy respectively. As outlined in our previous work [6], all the films have a preferred orientation along (002) planes indicating the c-axis orientation of the indium doped ZnO thin films. The intensity of the (002) peaks diminishes with the increasing indium content in ZnO. Microstructure of the grown films shows uniform distribution of grains throughout the film. The grain size decreases with the increasing indium concentration.

3.2. Gas sensing characteristics

The gas sensing characteristics of the grown films are studied in various toxic and combustible gas environments, such as H_2, CO and CH_4. The resistance transients for all the sensing elements are recorded at different operating temperatures (in the range 250- 380°C), in presence of all the mentioned gases and the response% is calculated. It was found that the response% increases with increase in operating temperature, attains its maximum value, and then decreases with further increase in the operating temperature. From the recorded response% optimum temperature (corresponding to the maximum response%) is noted. Now at the respective optimum temperatures, response% of all the sensing elements in presence of various concentrations of different gases (H_2, CO and CH_4) is also recorded. Fig. 1(a-c) shows the response and recovery transients for (a) H_2, (b) CO, (c) CH_4 (of various concentrations ~ (1660-200) ppm) measured at 350^{o}C for one typical sensor made out of 3 wt.% indium doped ZnO thin film. In a similar way, a number of transients for each of the above type of gases are recorded for all the gas sensors. Fig. 1(d) shows the response of these gases (~1660 ppm) measured at different operating temperatures ranging 250-380^{o}C. It indicates the optimum temperature for each gas to be 350°C.

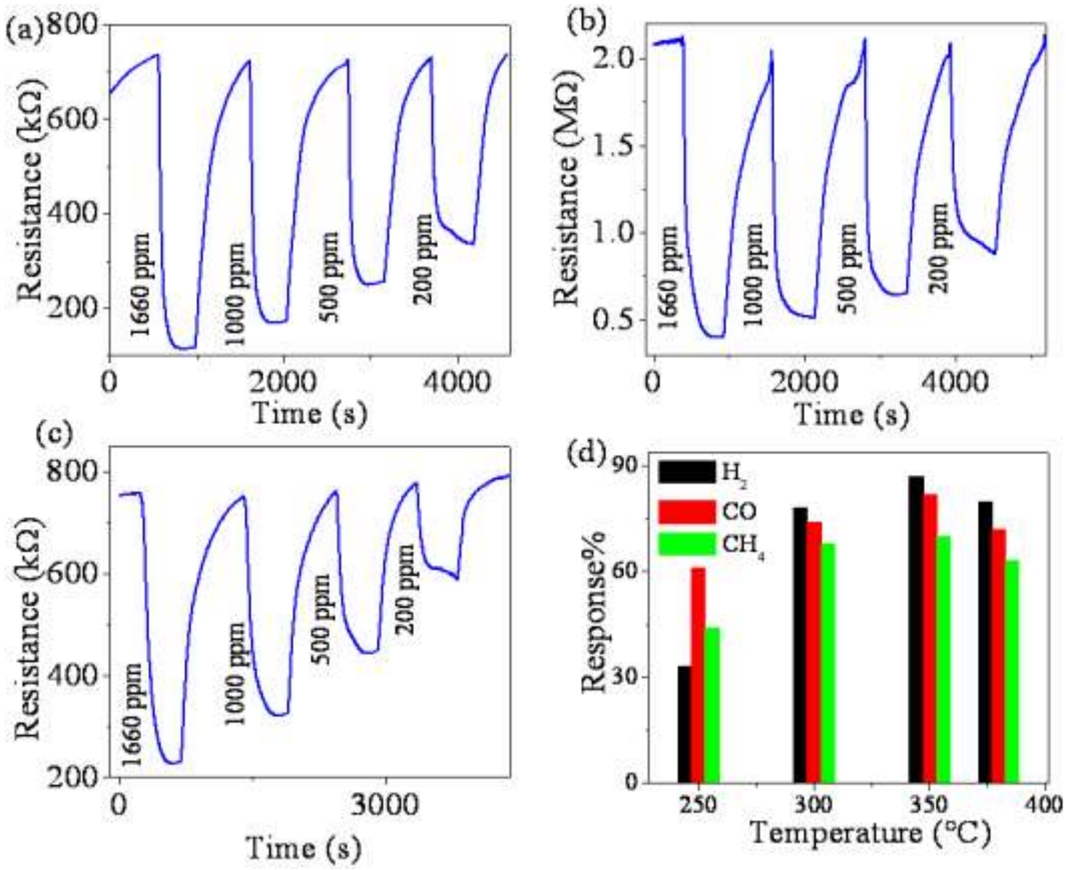

Fig. 1: Conductance transients during response and recovery of 3 wt.% indium doped ZnO thin film for various concentrations of (a) H_2, (b) CO, and (c) CH_4 sensing at the operating temperature ~ 350^{o}C. Fig. 1 (d) shows the response of the same film at various operating temperatures for a fixed concentration (~1660 ppm) of gases

Observing Fig. 1(a)-(c) it is clear that there is marginal conductance drift during response and recovery. From the figures it can also be observed that response% varies linearly with the gas concentration and the sensor is able to detect all the gases. From Fig. 1(d) it is clear that the indium doped ZnO thin film gas sensors are more sensitive to H_2 gas at all the operating temperatures, except 250°C, as compared to CO and CH_4 gas sensing. However, the cross selectivity of these gas sensors cannot be avoided simply by modulating the operating temperature, which imposes serious problem towards their commercial adaptability for making a selective gas sensor. To address the cross selectivity issue we have used FFT in conjunction with PCA as described below.

3.2.1. Feature Extraction from the Conductance Transients

After recording a number of transients for each of the above type of gas, the conductance transients are fast Fourier transformed (FFT) in order to extract the significant features. Through the fast Fourier transformation, the time domain conductance data is transformed into its frequency domain, which has the specific values for each different gas at different concentrations. For each test gas used in the present investigation, similar FFT is performed on their respective conductance transients. It is known that the low amplitude harmonics are affected by noise and hence do not carry significant information about the gas type. Therefore the low amplitude harmonics are discarded and only the low frequency part of the transformed harmonics is used for further analyses. Then, the amplitude of first 10 consecutive low frequency harmonics is extracted for different gases at each concentration and data matrix is constructed. The data matrices formed from FFT analyses are used as input in pattern recognition technique (principal component analysis (PCA)). The mathematical details of these analyses can be found elsewhere [10].

3.2.2. Pattern Recognition: Addressing the Selectivity of indium doped ZnO Thin Film Gas Sensors

The pattern recognition algorithms are used to address the cross selectivity issue of the semiconducting oxide gas sensors. Generally two types of algorithms are adopted for this purpose namely supervised and unsupervised. The most common unsupervised algorithm used in the pattern recognition technique is principal component analysis (PCA). It is a statistical tool which converts a data set of correlated variables to a set of uncorrelated variables termed as principal components (PCs). To use the PCA in gas sensor research, first the sensor response values are converted using available feature extraction techniques such as FFT. The selected coefficients of FFT are converted to principal components (PC_1 and PC_2) using PCA algorithm. Further details of these analyses can be found elsewhere [11].

In order to perform the PCA using FFT coefficients the following steps are adopted. A typical FFT input data is a 10 × 24 matrix (first ten Fourier coefficients and two conductance transients for each of three different gases at four concentrations have been considered). The dimension of this data matrix is then reduced by PCA. After reducing the dimension, the two components (principal component 2 vs. 1 (PC#2 vs. PC#1)) are plotted.

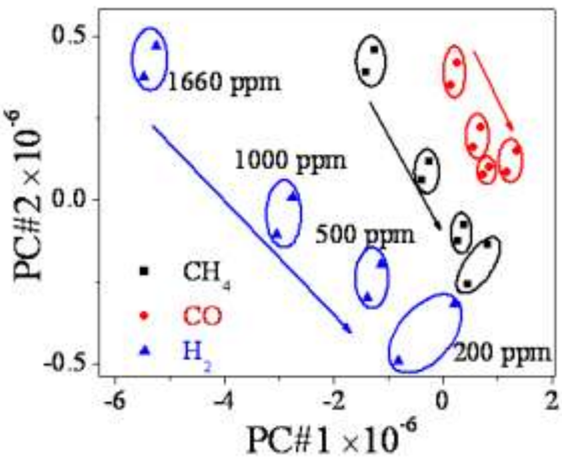

Fig. 2: Principal component analysis of the conductance transients of 3 wt. % indium doped ZnO thin film gas sensor, upon exposure of various concentrations of H_2, CO and CH_4, using FFT extraction parameter matrices

Fig. 2 shows the plot of PC#1 vs. PC#2 (estimated from the principal component analyses) for 3 wt.% indium doped ZnO thin film sensing element in presence of three different gases at various concentrations. As observed from the Fig. 2 all the gases form well distinct clusters at each ppm, indicating the discrimination of different gases at various concentrations. So it can be said that PCA using FFT can be useful in studying the selectivity issue of these gas sensors.

4. Conclusion

Indium doped ZnO thin films are synthesized using sol gel spin coating technique. Structural and micro structural characteristics of the grown films are investigated form XRD pattern and FESEM images respectively. Gas sensing characteristics for all the sensing elements are studied using various concentrations of different toxic and combustible gases, such as H_2, CO and CH_4, at different operating temperatures. To study the cross selectivity of the sensors pattern recognition technique is adopted. From PCA analyses it is observed that individual gases at each ppm level form well distinct clusters. From the observed results it is said that PCA using FFT yield promising results in selective detection of the gases.

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