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# Examining the effects of polymer binder in Fe<sub>2</sub>O<sub>3</sub>/ZnO thick film sensors on the response to propanol vapour

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**Abstract:** Investigations have been carried out on the role of the binder in screen printed Fe<sub>2</sub>O<sub>3</sub>/ZnO thick film sensors for gas and vapour analysis. These sensors were prepared by mixing a polymer binder and carbon black with a 50:50 Fe<sub>2</sub>O<sub>3</sub>/ZnO mixture which has been previously fired at 1250°C. The advantages of these sensors include room temperature operation, straight forward circuitry and low power consumption. Previous work in the literature has concentrated on varying the composition of the oxides in the sensing layer to improve their sensitivity to vapours. The aim of this study is to evaluate the contribution of the polymer binder to the sensor response and selectivity. The polymer binders investigated were Ethyl Cellulose (EC) and polyvinyl butyral (PVB). Sensors were prepared using each binder and exposed to propanol at concentrations ranging from 500-14000 ppm in an automated dynamic flow system. Drop coated PVB and EC sensors containing carbon black (CB) were also fabricated in order to compare their responses with the thick film oxide sensors. Correlations were found between both sensor types suggesting that the polymer binder plays a significant role in the response mechanism of room temperature oxide sensors.

## 1. INTRODUCTION

As concern for environmental safety rises, so too does the need for fast, accurate low powered gas sensors. Interest has grown in the use of metal oxide gas and vapour sensing devices for applications such as air quality control, remote sensing of toxic environmental pollutants and industrial environmental control [1-3]. The sensitivity, selectivity and stability of these materials make them ideal candidates for gas sensing applications. Previous work has explored the use of oxide materials such as ZnO, TiO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> in gas sensing devices. Multi-component oxides like NiFe<sub>2</sub>O<sub>4</sub>, SrFe<sub>2</sub>O<sub>3</sub> and ZnFe<sub>2</sub>O<sub>4</sub> have also been successfully used in gas sensing applications [4, 5].

These studies have concentrated on using the chemical make up of the oxide material, its structural defects and grain size to describe the degree of sensitivity of the material to a particular gas. However an inherent disadvantage to metal oxide sensors is their operation at elevated temperatures which requires the printing of a heating element on the back on the sensor. This contributes to an increase in

power consumption, fabrication costs as well as complexity in sensor design [6]. However recent studies have shown that mixing the oxides with a polymer binder allows for room temperature operation [4].

Various approaches have been used to produce oxide gas sensors including thin film techniques, thermal deposition, sputtering and solgels and thick film techniques, screen-printing and drop coating. This study focuses on the use of screen-printing to produce the oxide sensors.

Screen printing is a thick film technology that uses a squeegee to force a paste through the apertures of a stencil screen to form a pattern on the substrate. Paste preparation involves the mixing of oxide particles with a polymer binder and suitable solvent. Generally the role of the polymer binder in the response mechanism of the sensor is ignored and the sensitivity is explained with reference to the oxide interaction with the vapour. This study investigates the role of the polymer binder in the sensor response mechanism and determines whether it can be used as a means to alter the sensitivity and selectivity of the sensor.

## 2. EXPERIMENTAL

### 2.1 Paste preparation and sensor fabrication

Thick film paste preparation was carried out using 50:50 mol. %  $\text{Fe}_2\text{O}_3/\text{ZnO}$  powders that had been wet-ball milled in alcohol for 24hr and dried at  $120^\circ\text{C}$ . This powder was then pressed into a pellet under 2 tons of pressure and fired at  $1250^\circ\text{C}$  for 5 hrs under  $6 \times 10^{-3}$  mbar vacuum, heated at a rate of  $5^\circ\text{C}/\text{min}$ , and cooled at the rate of  $3^\circ\text{C}/\text{min}$ . These fired pellets were then broken into a fine powder using a Gy-RO Mill machine for 10 mins.

This powder was mixed into a paste with 5 wt.% polymer binder and 1.5 wt.% carbon black using ethylenglycolmonobutylether as a solvent. The two polymer binders investigated in this study were ethyl cellulose (EC) and polyvinyl butyral (PVB). Sensors were fabrication by screen-printing these pastes onto alumina substrates with copper interdigitated electrode patterns. The method for electrode fabrication has been reported elsewhere [7]. These thick film sensors were then left to dry in an oven at  $80^\circ\text{C}$  for 30 mins.

Drop coated sensors were also prepared using the same ratio of polymer to CB for the thick film pastes. A  $0.1\mu\text{L}$  drop of material was deposited onto interdigitated electrode patterns using an in house designed drop coating apparatus [8].

### 2.2 Gas chamber apparatus and sensor exposure

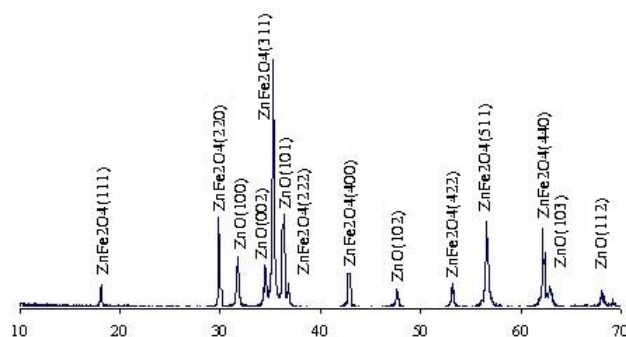
A specifically designed dynamic flow gas test chamber was utilized to expose the thick film arrays to propanol at specific vapour concentrations. The chamber uses a Bronkhorst EL-Flow mass flow meter/controller to control the carrier gas and a  $\mu$ -Flow liquid mass flow meter with a Controlled Evaporator Mixer (CEM). The liquid and gas flow controllers were manually operated using an EZ-7000 controller unit and the system was connected to a PC for automatic operation. The array was first flushed for 60 mins to obtain a stable baseline resistance. The sensors were exposed to propanol vapour in concentrations from 2500-5000 ppm in increasing steps of 500 ppm. The exposure cycle consists of a 30 secs flush with a 60 secs exposure followed by another 30 secs flush. The consequent voltage change on exposure was recorded using a National Instruments data acquisitions card (Model No: PCI-MIO-16E-4) and LabVIEW software.

## 3. RESULTS AND DISCUSSION

### 3.1. Material Properties

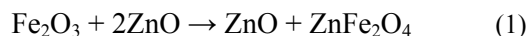
#### 3.1.1 X-ray diffraction analysis

The processes such as milling and firing are known to cause changes in material composition. An analysis was therefore carried out on the composition of the powders using X-ray diffraction.



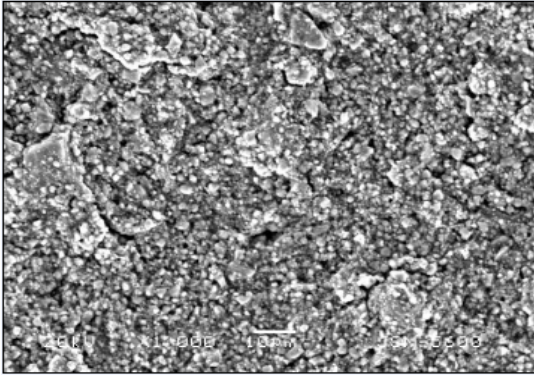
**Fig. 1.** X-ray diffraction pattern from  $10^\circ$  to  $70^\circ$ ,  $2\theta$ , of 50% mol.  $\text{Fe}_2\text{O}_3$  / 50% mol.  $\text{ZnO}$

The results show that the final composition of the powder after firing contains two phases the main phase being  $\text{ZnFe}_2\text{O}_4$  and the second phase being  $\text{ZnO}$ . This was confirmed by referring to JCPDF files card no: (77-0011) and (01-1136) for  $\text{ZnFe}_2\text{O}_4$  and  $\text{ZnO}$  respectively. According to this data the chemical reaction taking place during the firing process at  $1250^\circ\text{C}$  under vacuum can be explained by Eq. (1).



#### 3.1.2 Scanning electron microscopy

Scanning electron microscopy images were obtained of the screen printed sensing layers for direct comparison between the sensors containing EC and sensors containing PVB. The SEM micrograph in Fig. 2 illustrates the surface morphology of the thick film oxide sensor containing PVB binder. This SEM is similar to the image obtained from the thick film oxide sensor containing EC indicating that the both polymers have a similar effect on the morphology of the sensing layer.

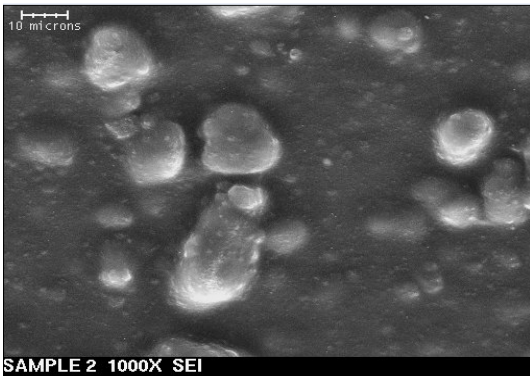


**Fig. 2.** SEM micrograph of thick film oxide PVB sensing layer – Magnification 1000x

In order to examine the morphology of the polymer and carbon black two thick film sensors were fabricated containing the same ratio of polymer to carbon black as was used to prepare the Fe<sub>2</sub>O<sub>3</sub>:ZnO sensors. The resulting SEM images are illustrated in Fig. 3 and Fig. 4.

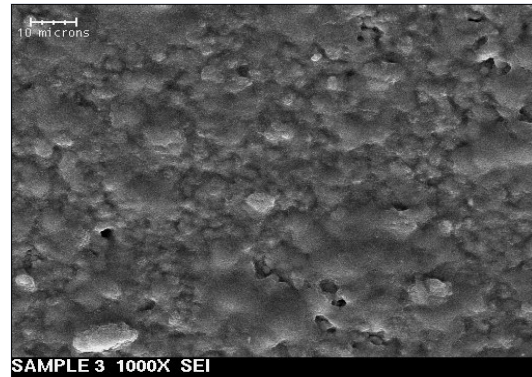


**Fig. 3.** SEM micrograph of thick film EC sensing layer – Magnification 1000x.

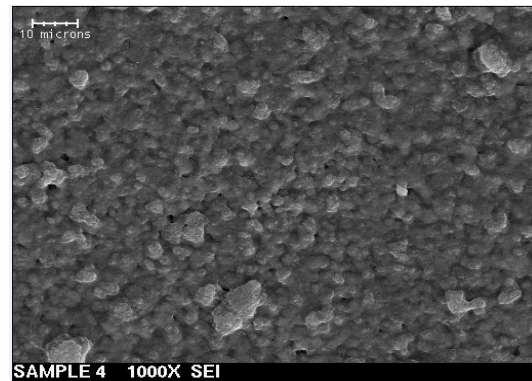


**Fig. 4.** SEM micrograph of thick film PVB sensing layer – Magnification 1000x

Two drop coated sensors were also fabricated with PVB/CB and EC/CB. The SEM images of these sensors are shown in Fig. 5 and Fig. 6.



**Fig. 5.** SEM micrograph of drop coated EC sensing layer – Magnification 1000x.



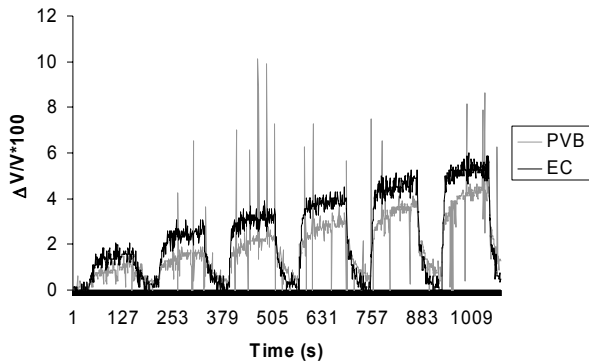
**Fig. 6.** SEM micrograph of drop coated PVB sensing layer – Magnification 1000x.

It can be seen from Fig. 3-6 that the EC films prepared using both thick film and drop coating techniques are more uniform than their PVB counterparts.

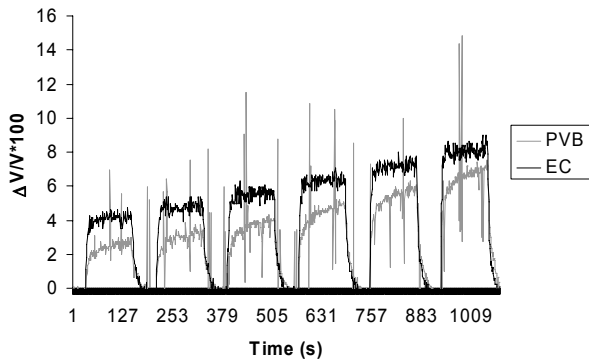
### 3.1.3 Sensor response to propanol

An automated test chamber was used to expose the thick film oxide sensor array to specific concentrations of propanol from 500-1400 ppm. The relative differential change in the voltage reading from each sensor was calculated using Eq. (2).

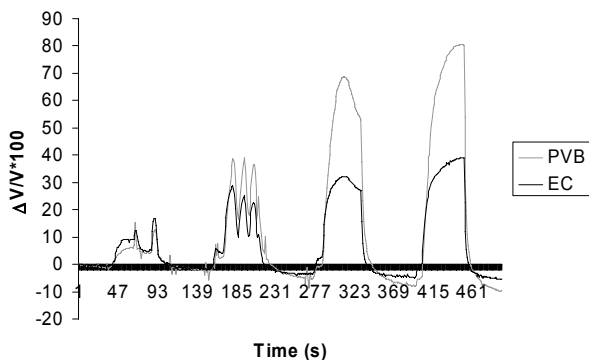
$$\frac{\Delta V}{V} \% = \left( \frac{V_{vapour} - V_0}{V_0} \right) \times 100 \quad (2)$$



**Fig. 7.** Response curves for thick film oxide sensors containing EC and PVB binders when exposed to 500-3000 ppm of propanol in steps of 500 ppm



**Fig. 8.** Response curves for thick film oxide sensors containing EC and PVB binders when exposed to 2500-5000 ppm of propanol in steps of 500 ppm



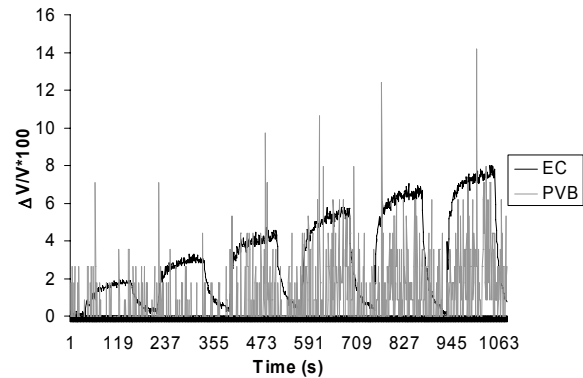
**Fig. 9.** Response curves for thick film oxide sensors containing EC and PVB binders when exposed to 5000-14000 ppm of propanol in steps of 3000 ppm

It can be seen from Fig. 7 and Fig. 8 that both thick film oxide sensors containing EC and PVB binders show a linear increase in response with increasing

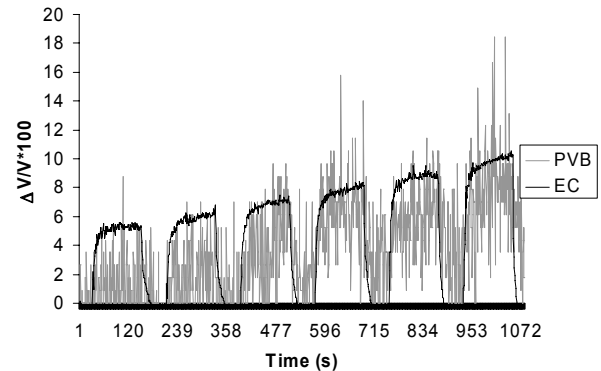
concentration of propanol vapour at concentrations ranging from 500-5000 ppm. Fig. 7 and Fig. 8 also show that EC has a greater sensitivity to propanol at these concentrations when compared to the noisy responses obtained from PVB. However Fig. 9 shows that at concentrations greater than this the sensor with PVB binder shows a greater sensitivity and a large reduction in noise levels.

### 3.1.4 Drop coated polymer/CB sensors

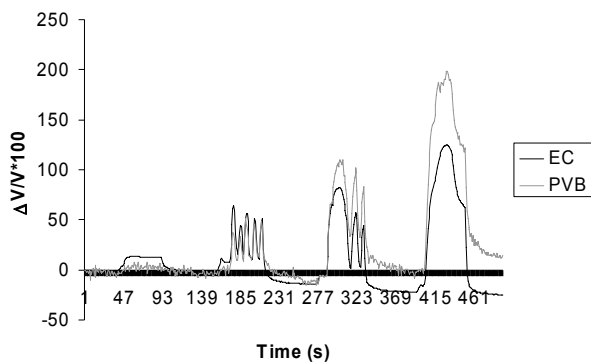
Drop coated polymer/CB sensors were fabricated for direct comparison with the thick film oxide sensors. These sensors were exposed to the same concentrations of propanol and the results obtained are shown in Fig. 10-12.



**Fig. 10.** Response curves for drop coated EC/CB and PVB/CB sensors when exposed to 500-3000 ppm of propanol in steps of 500 ppm



**Fig. 11.** Response curves for drop coated EC/CB and PVB/CB sensors when exposed to 2500-5000 ppm of propanol in steps of 500 ppm



**Fig. 12.** Response curves for drop coated EC/CB and PVB/CB sensors when exposed to 5000-14000 ppm of propanol in steps of 3000 ppm

The drop coated EC sensor showed a linear increase in response from 500-5000 ppm similar to the response obtained from its thick film counterpart. The PVB sensor at this concentration range showed very noisy responses well below the signal to noise ratio threshold for sensor devices. Above this concentration range however, PVB starts to show a high signal to noise ratio and begins to produce responses higher than that obtained by EC for the same concentration levels.

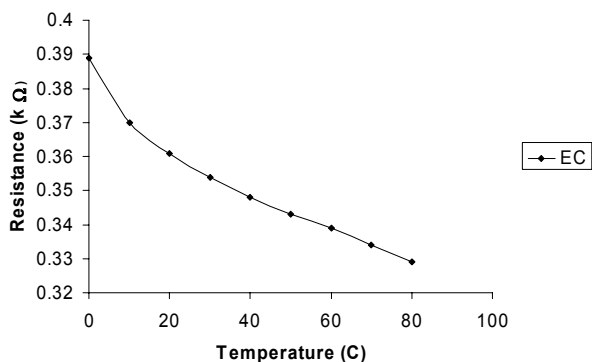
Comparing the results obtained from the drop coated sensors, Figs. 10-12, with the thick film oxide sensors, Figs. 7-9, it can be seen that sensors containing EC show larger responses at low ppm levels than their PVB counterparts. The higher sensitivity of EC sensors can be attributed to a more uniform film as seen in Fig. 3 and Fig. 5 and homogenous dispersion of CB.

PVB sensors have shown poor dispersion of CB and a non-uniform layer as seen in Fig. 4 and Fig. 6. This also explains the excess noise in the response of these sensors. An inhomogeneous layer gives rise to non-uniform current paths, causing fluctuations in the conduction through the material [8, 9]. At low concentrations, movement of heterogeneously dispersed agglomerated CB particles causes noise fluctuations due to the continuous forming and breaking of conduction paths. At concentrations above 5000 ppm the noise is dramatically reduced as the level of polymer expansion is high enough to separate the agglomerated CB particles. This also contributes to the increase in the response of PVB sensors about 5000 ppm.

The use of different polymer binders was seen to alter the percentage response of the sensor. This shows that the selectivity and sensitivity of the sensors could be altered depending on the chemical structure of the polymer binder used. This indicates that the polymer binder plays an important role in the response mechanism of low temperature thick film oxide sensors and it can be chosen specifically for detection of a particular vapour.

### 2.3 Temperature analysis

It is important in gas sensing applications to know the effect of temperature on sensor output especially for applications such as environmental monitoring where the temperature may fluctuate substantially [10]. The effect of temperature on the baseline resistance of the thick film oxide sensors was analysed using in house designed test equipment. The results showed that both sensors have negative temperature coefficients (NTC), whereby the resistance of the material decreases for an increase in temperature. The results are illustrated in Fig. 13 and Fig. 14.

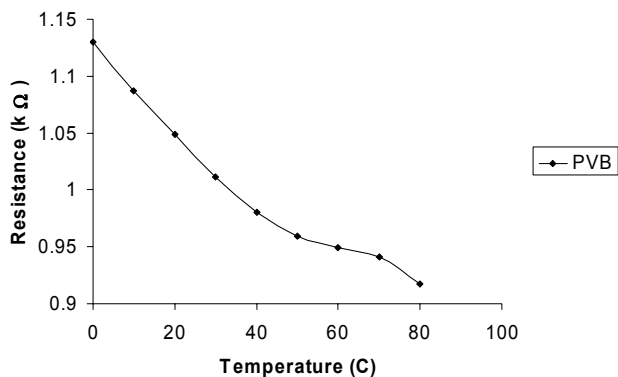


**Fig. 13.** The effect of temperature on the baseline resistances of thick film oxide sensors with EC binders

The temperature coefficient of resistance (TCR), which is a measure of the parts per million change in resistance for every 1°C change in temperature was calculated according to Eq. (3).

$$TCR = \frac{R_{t1} - R_{t2}}{R_{t1} \Delta T} \times 10^6 \quad (3)$$

where  $R_{t1}$  is the resistance at temperature 1,  $R_{t2}$  is the resistance at temperature 2, and  $\Delta T$  is the change in temperature.



**Fig. 14.** The effect of temperature on the baseline resistances of thick film oxide sensors with PVB binders

The TCR values calculated are illustrated in Tab. 1.

	TCR (ppm/°C)	
	Region 1 (5-20°C)	Region 2 (20-80°C)
EC	$2.63 \times 10^6$	$2.72 \times 10^6$
PVB	$0.90 \times 10^6$	$0.95 \times 10^6$

**Tab. 1.** TCR values for thick film oxide sensors containing EC and PVB binders

It can be seen from Tab. 1 that the oxide sensors containing EC has a higher TCR value which indicates a higher sensitivity to temperature fluctuations.

## CONCLUSION

The effects of EC and PVB polymer binders on the response of Fe<sub>2</sub>O<sub>3</sub>/ZnO thick film sensors were investigated. Both sensor compositions gave linear responses to propanol at concentrations ranging from 500-5000 ppm. However the responses produced by PVB sensors are very noisy at these concentrations. The PVB sensors show a sudden reduction in noise and a large increase in sensitivity at concentrations above 5000 ppm. This study has shown that the sensitivity and stability of thick film oxide sensors can be manipulated through careful selection of the polymer binder.

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