

# NiO-TiO<sub>2</sub> thick-films for detection of alcohol vapours at room temperature

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## Abstract

The response of screen-printed thick-films of NiO/TiO<sub>2</sub> to organic solvent vapours was studied. It was found that these films displayed a significant resistance change in response to the vapours even at room temperature. The sensors displayed an inherent selectivity, proving most sensitive to toluene and propanol vapour; with comparatively low responses exhibited towards ethanol and methanol vapours. Very fast response and recovery times of 9s and 16s respectively were recorded for the devices upon exposure to 4,000ppm step changes in propanol concentration.

## Keywords

Nickel oxide; Titanium dioxide; Gas sensor; Thick film; Polymer; Binder

## INTRODUCTION

Highly sensitive and selective alcohol sensors are in constant demand in the chemical, biomedical and food industries and also for the advancement of electronic nose technology. The majority of oxide based semiconductor gas sensors require heaters as they are operated at elevated temperatures – typically 200-500°C. This not only increases the power consumption of the device but also adds to the fabrication cost and complexity. In order to facilitate the portable and real-time measurement and classification of gases, low power sensors that can operate at room temperatures are the focus of much recent research [1].

Nickel oxide (NiO) and titanium dioxide (TiO<sub>2</sub>) films have individually proven successful in gas sensing applications [2, 3]. This study investigates the use of combined NiO-TiO<sub>2</sub> thick-films for the detection of alcohol vapours at room temperature. A screen-printing process was used to fabricate the sensors.

## EXPERIMENTAL

In order to fabricate the thick-film devices, pastes were prepared from a 74.5%/25%/0.5% mol.% NiO/TiO<sub>2</sub>/carbon respectively. The carbon was added to decrease the baseline resistance of the films. Poly(vinyl buterol) (PVB) was used as a permanent binder and constituted 5% of the total weight of the samples, while ethylenglycolmonobutylether was used as the solvent. The paste was screen-printed onto a (pre-printed) silver interdigitated electrode pattern on glass substrates, with an electrode gap of 0.4mm. Finally the samples were cured in an oven at 110°C for one hour.

For comparative tests, devices were fabricated from a 50%/50% w/w mixture of PVB to carbon black (CB). Tetrahydrofuran (THF) was chosen as a solvent and in order to obtain a homogenous, well-dispersed suspension, the mixture was shear mixed for 15 minutes prior to deposition. Using a micro-litre pipette the composites were deposited onto substrates with interdigitated electrode patterns identical to the ones used for the thick-film devices. The average volume of the composite deposited was 4μL.

## Testing Apparatus

The response of the devices to the various organic solvent vapours was measured using a gas chamber (volume 2,000cc). A schematic diagram of the test chamber is shown in Figure 1.

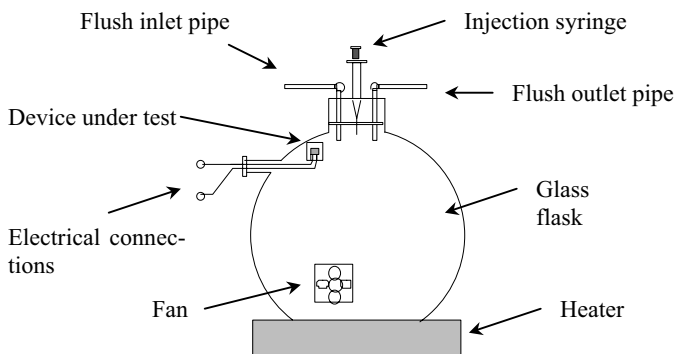


Figure 1. Schematic diagram of the chamber used to test the gas sensors.

The resistance of the devices was measured using a Thurlby Thandar Ohmmeter (model no: 1705). A Sloan Dektak profilometer (model no: 900051) was used to measure the thickness of the sensing layers.

## RESULTS AND DISCUSSION

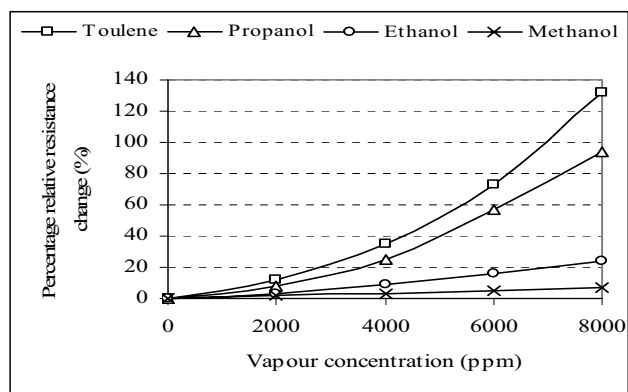
### Sensor Responses to Alcohol Vapours

In this study, the percentage relative change in resistance was measured:

$$\frac{\Delta R}{R} \% = \left( \frac{R_{vapour} - R_0}{R_0} \right) \times 100 \quad (1)$$

where  $R_{vapour}$  is the sensor resistance upon its exposure to alcohol vapour and  $R_0$  is the sensor baseline resistance.

The room temperature response of the screen-printed NiO-TiO<sub>2</sub> devices to methanol, ethanol, propanol and toluene vapours is shown in Figure 2.



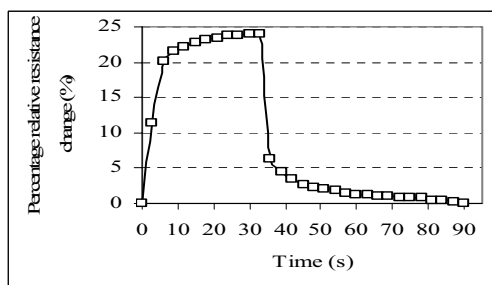
**Figure 2. Response of the NiO-TiO<sub>2</sub> films with increasing vapour concentration.**

It can be seen from Figure 2 that the devices display a significant response to the vapours tested at room temperature.

It can also be seen from Figure 2 that the sensors show a range of sensitivities to the vapours tested. In order of decreasing sensitivity, the highest sensor response was to toluene vapour, followed by propanol, ethanol and methanol vapour respectively.

#### Response and Recovery Times

For this analysis, the response time is defined as the time it takes for the sensor under test to reach 90% of the maximum saturated conductance value following a step change in gas concentration, while the recovery time is the time it takes to return to 10% of the saturated value. The devices were exposed to a 0-4,000ppm step change in propanol concentration (at  $t=0s$ ), subsequently, upon reaching their steady state response, the vapour was flushed from the chamber. Figure 3 shows the fast response and recovery characteristics observed.



**Figure 3. Response and recovery characteristics of the thick-film NiO-TiO<sub>2</sub> device.**

From Figure 3 it is evident that the NiO-TiO<sub>2</sub> film exhibits extremely fast response and recovery times; measured at 9s and 16s respectively.

#### Effect of Carbon Loading on Sensitivity

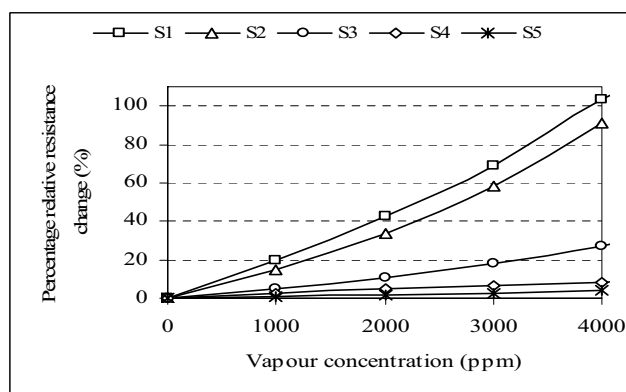
To assess the effect of the carbon loading on the vapour sensing characteristics, the percentage molecular weight of

carbon was varied in the screen-printed devices. Table 1 indicates how these variations were made. (Note that device S3 was the original device used in obtaining the results presented above.)

**Table 1. Molecular weight ratios of materials used to NiO-TiO<sub>2</sub> thick-film devices.**

Device Name	Composition Ratio (% Mwt)		
	NiO	TiO <sub>2</sub>	C
S1	75%	25%	0%
S2	74.99%	25%	0.01%
S3	74.95%	25%	0.05%
S4	74.5%	25%	0.5%
S5	74%	25%	1%

Figure 4 presents the responses of the devices detailed in Table 1 to propanol vapour.



**Figure 4. Response of devices with varying carbon content to propanol vapour.**

The purpose of adding the carbon was to improve the baseline resistance of the devices. This proved to be justified, as although it can be seen from Figure 4 that increasing carbon content resulted in decreasing device sensitivity, accurate and sufficiently stable baselines were difficult to obtain for the low-to-zero carbon content devices (S1 and S2).

#### The Sensing Mechanism

In all cases the sensors exhibited an increase in resistance upon exposure to the alcohol vapours, this suggested that the metal-oxide layers were behaving as expected from p-type semiconductors in response to a reducing gas. In a p-type semiconducting oxide, adsorbed oxygen behaves as a surface acceptor state, trapping electrons from the valence band and hence increasing the hole concentration. The general case of a reducing gas interacting with the adsorbed oxygen at the sensor surface can be explained by the following reaction:



where  $R$  is the reducing gas,  $O_{(ads)}^-$  is the oxygen ion adsorption and  $e^-$  are freed electrons. To maintain neutrality

of charge, the freed electrons are re-injected into the semi-conducting oxide, which results in a decrease in the hole concentration and hence an increase in resistance of the sensor is observed [4]. The magnitude of reaction (2) determines the sensor's sensitivity to a particular reducing gas. However, for the NiO-TiO<sub>2</sub> thick-film devices under examination in this study, other factors may be the reason for the different sensitivities exhibited by the sensors to the vapours tested – these factors will subsequently be proposed and discussed.

### The Influence of the Polymer Binder

The use of polymer binders is a standard practice in the preparation of thick-film pastes. Recall from the experimental section that a polymer (PVB) was used as a binder to bind the functional materials (oxides) together during device fabrication. However, polymer composites themselves have found use as gas sensitive resistors. The permeation of vapours into polymer composites can lead to swelling of the structure. This effect on the polymer matrix is related to polymer/solvent interactions, which is in turn described by the Flory – Huggins interaction parameter – see Equation 3.

$$\chi_{12} = \frac{V_s}{RT} (\delta_s - \delta_p)^2 \quad (3)$$

where  $V_s$  is the molar volume of the solvent (cm<sup>3</sup>/mol<sup>-1</sup>),  $T$  the temperature (K),  $R=8.314\text{Jmol}^{-1}$ ,  $\delta_s$  the solvent solubility (J<sup>1/2</sup>cm<sup>-3/2</sup>) and  $\delta_p$  the polymer solubility (J<sup>1/2</sup>cm<sup>-3/2</sup>). A good solubility of the polymer into the solvent is obtained for low or null values of  $\chi_{12}$  [5]. It may be concluded then, that the lower the quantity  $(\delta_s - \delta_p)^2$ , the better the interaction between the polymer and solvent [6].

The  $\delta_p$  value for PVB is calculated as 18.4, Table 2 presents calculations of the quantity  $(\delta_s - \delta_p)^2$  of the  $\delta_s$  values of the four organic vapours tested.

**Table 2. Calculations based on solubility parameters of PVB and organic solvents used in tests.**

Solvent	$\delta_s$	$(\delta_s - \delta_p)^2$
Toulene	18.2	0.04
Propanol	24.4	36
Ethanol	25.6	51.84
Methanol	29.7	127.69

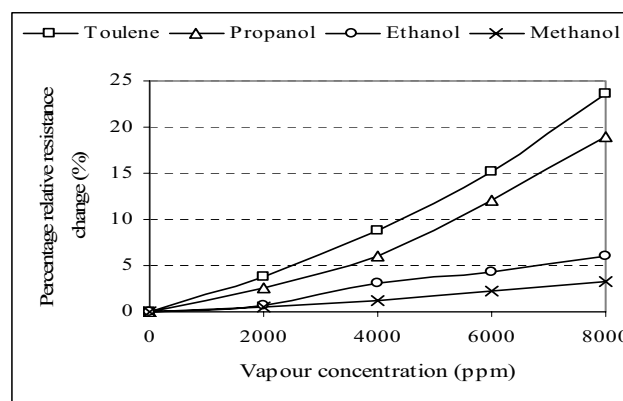
It can be seen from Table 2 that the degree of solubility of PVB in the solvents is highest (lowest value of  $(\delta_s - \delta_p)^2$ ) for toluene, followed by propanol, then ethanol and methanol respectively. This is the same order as the responses (highest to lowest response) observed from the thick-film NiO-TiO<sub>2</sub> devices – refer to Figure 2.

Hence, it is proposed that the binder used in the fabrication of the NiO-TiO<sub>2</sub> screen-printed devices is having a profound effect on the degree of sensitivity exhibited by the sensors to the individual organic vapours. The binder

(PVB) may be contributing significantly to the sensitivity to the individual organic vapours by controlling the degree of interaction between the vapour and the functional oxides (NiO/TiO<sub>2</sub>) and hence govern the magnitude of the reaction described in (2).

### Response of PVB\CB Devices to Organic Vapours

To confirm the theoretical results based on the solubility parameter calculations of Table 2, a PVB\CB composite sensor was fabricated and tested with the selected set of vapours. Figure 5 shows the response of the PVB\CB device upon exposure to the vapours.



**Figure 5. Response of the PVB\CB device with increasing vapour concentration.**

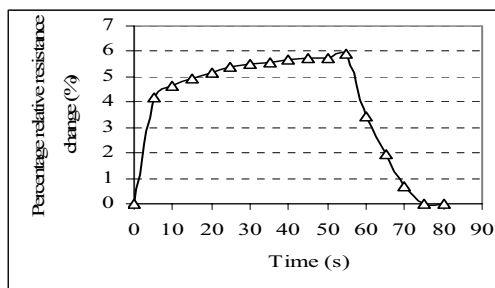
From Figure 5 it can be seen that the expected result is confirmed, in that the order of sensitivity to the four vapours is identical to that of Figure 2 and as predicted by the calculations of Table 2.

In comparing the results of the thick-film NiO-TiO<sub>2</sub> device (Figure 2) and the PVB\CB device (Figure 5), it can be seen that the NiO-TiO<sub>2</sub> sensors display a significantly superior sensitivity to all the organic vapours. This might be considered a surprising result, since according to profilometer measurements; the NiO-TiO<sub>2</sub> devices were measured as being approximately seven times thicker than the PVB\CB devices, due to their different fabrication methods.

To explain this result, it is suggested that the thick-film devices achieve a very high surface area to bulk ratio, i.e. high porosity or free volume, when the oxides were present in the polymer matrix. This occurs when incompatible particles are dispersed in a polymer, voids tend to occur at the interface, which leads to an increase in the free volume and hence an increase in the diffusion of vapours into the material [7]. For gas sensors, high porosity results in a larger specific surface area, which consequentially increases the sensitivity of the device [8].

Moreover, it was observed that increasing carbon content resulted in decreasing device sensitivity. As carbon is a filler which is highly compatible with the polymer matrix, it will have the effect of taking up the free volume within the structure, hence reducing the device porosity [7], this

could be the cause of the observed decrease in the sensitivity. This may be considered further proof that a more open and porous structure is a primary contributing factor to the superior sensitivity of the thick-film device.



**Figure 6. Response and recovery characteristics of the PVB/CB devices.**

Figure 6 shows the response and recovery characteristics of the PVB/CB film, which are measured at 23s and 24s respectively. These times are not as quick as the response and recovery times of the NiO-TiO<sub>2</sub> sensors, again this may be attributed to the more porous structure attained by the NiO-TiO<sub>2</sub> films, as porosity is also a critical factor in optimising the speed of sensor response [9].

#### Effect of Different Oxides

As part of this study, and drawing on the results of previous studies [10], sensors were fabricated using a similar procedure (screen-printed and containing PVB binders) with different metal-oxide materials. Cuprous oxide (Cu<sub>2</sub>O) and ratios of iron-oxide/zinc-oxide (Fe<sub>2</sub>O<sub>3</sub>/ZnO) were used. The devices fabricated displayed different sensitivities in response to the organic vapour set. However, in all cases, the order of the sensitivities was identical to the order in this study. This again provides further evidence as to the possible role the binder material plays in governing the magnitude of sensor response and the selectivity to different organic compounds according to their solubility parameters.

#### CONCLUSION

It has been demonstrated that NiO-TiO<sub>2</sub> thick-films can function as sensitive alcohol vapour sensors. The sensors have been shown to operate effectively at room temperature, which is a distinct advantage over other semiconducting oxide based devices that require a heater to function efficiently. The sensors displayed an inherent selectivity, proving most sensitive to toluene vapour, then propanol vapour, with the lowest sensitivities in response to ethanol and methanol vapour respectively. It was proposed that the polymer binder used in the fabrication of the NiO-TiO<sub>2</sub> thick-films, was a significant factor in controlling the sen-

sor sensitivity to the individual organic vapours of different solubility parameters.

The response and recovery times were measured at 9s and 16s respectively. These times are extremely fast in comparison to previous values reported for thick-film devices. The superior sensitivities and response times of the thick-film sensors were attributed to a large specific surface area, due primarily to the highly porous structure of the thick-film devices, caused by the excessive free-volume induced in the polymer-binder matrix by the oxide materials.

#### ACKNOWLEDGMENTS

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