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Heterojunction gas sensors for environmental NO_2 and CO_2 monitoring

Z. Ling, C. Leach, R. Freer *

Manchester Materials Science Centre, University of Manchester and UMIST, Grosvenor Street, Manchester M1 7HS, UK

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Abstract

The NO_2 and CO_2 sensing properties of a heterojunction gas sensor formed between *n*-type ZnO and a *p*-type composite based on a mixture of $BaTiO_3/CuO/La_2O_3$ have been evaluated and compared with the performance of its component *p*- and *n*-type materials. It was found that the individual ZnO and $BaTiO_3/CuO/La_2O_3$ sensors showed resistance increases when exposed to NO_2. When exposed to CO_2, the ZnO based sensor showed no response, while the $BaTiO_3/CuO/La_2O_3$ sensor showed a small resistance increase. The heterojunction sensor was found to be insensitive to <3000 ppm CO_2 although at higher concentrations it showed a small decrease in resistance. The resistance also decreased when exposed to low levels of NO_2, indicating that a different detection mechanism was operative at the heterocontact compared with the single-phase materials.

Keywords: $BaTiO_3$ and titanates; Electrical properties; Sensors; Interfaces; ZnO

1. Introduction

The global gas sensor market is currently dominated by America and Japan, who together account for over 90% of the products sold.[1] Solid-state gas sensors, fabricated from a single-phase semiconducting ceramic, are a compact, low-cost form of sensor that can be used to detect target gases through changes in electrical properties brought about by surface reactions associated with the adsorption of gases. However, they generally have a low selectivity to specific target gases, high power demands and require periodic high temperature cleaning cycles in-service to remove the surface adsorbed layer and maintain performance.[1]

Heterojunction gas sensors are a novel class of solid state gas sensors that attempt to overcome the inherent problems of existing monolithic gas sensors through the introduction of smart functions including tuneable selectivity, self-cleaning properties and an in-built failure detection mechanism.[2,3] Geometrically, heterojunction gas sensors consist of two semiconducting oxides in contact, and the active region is the interface between the two materials, which behaves like a *p–n* junction. Gases adsorbed on either side of the heterocontact are oxidised at varying rates at the heterojunction interface and influence its rectifying characteristics.[4] Since a loss of rectifying characteristics implies breakdown of the *p–n* junction, there is an in-built failure detection mechanism.[5,6] The sensing properties of junctions based on *n*-type zinc oxide and a *p*-type component based on a doped copper oxide or perovskite phase such as La_2CuO_4 have been reported.[7]

The sensitivity and selectivity of the sensor to the target gases varies with the addition of certain dopants[5,6] and the interrogation method used, enabling a variety of measurements to be made and providing a range of complementary signals from gas mixtures that may be resolved in software.

In this contribution the sensitivity of a heterojunction between ZnO (*n*-type) and a mixture of $BaTiO_3/CuO + 3\%$ La_2O_3 (*p*-type) to NO_2 is presented and compared with the performance of the constituent materials. The formulation, $BaTiO_3/CuO + 3\%$ La_2O_3, has been reported as a capacitative CO_2 sensor,[8] although its NO_2 sensing properties have not previously been considered.

* Corresponding author. Tel.: +44-161-200-3564; fax: +44-161-200-3586.

E-mail address: robert.freer@umist.ac.uk (R. Freer).

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2. Method

All tests were carried out on sensors formed from sintered pellets. For the zinc oxide sensor GPR grade ZnO powder was compacted and sintered at 700°C for 5 h to produce a pellet with a density of 93% of theoretical. The $BaTiO_3/CuO/La_2O_3$ sensor was prepared by mechanically mixing the constituent powders in propan-2-ol in the proportion 0.485:0.485:0.03 by weight, followed by drying, compaction and sintering at 1000C for 5 h to produce a pellet with a density 56% of theoretical.

Sensors based on the individual pellets were prepared by screen-printing silver electrodes on opposite faces and attaching platinum lead out wires. The heterojunction sensor was prepared by clamping together faces of the constituent pellets that had been roughened to permit gas permeation along the interface (Fig. 1). The sensors were placed into a controlled atmosphere furnace providing ambient and reducing gas environments (Fig. 2). Compressed air was used as a carrier gas to which 0–10 ppm NO_2 or 0-5000 ppm CO_2 was added from a second cylinder whilst maintaining a constant flow rate of 100 cm^3 min^{-1}.

Electrical measurements were made using a Thurlby 6512 voltage source and a Fluka 8010A multimeter, both of which were fitted with a IEEE interface to permit automatic data logging via a computer.

3. Results and discussion

Fig. 3(a) shows a scanning electron microscope (SEM) image of the surface of the zinc oxide sensor and Fig. 3(b) the surface of the $BaTiO_3/CuO/La_2O_3$ sensor.

Sensor performance was assessed by making a series of current–voltage (I–V) and resistance–time (R–T) measurements at an optimised temperature of 300°C. The responses of the individual sensors and the heterojunction sensor to CO_2 and NO_2 were assessed.

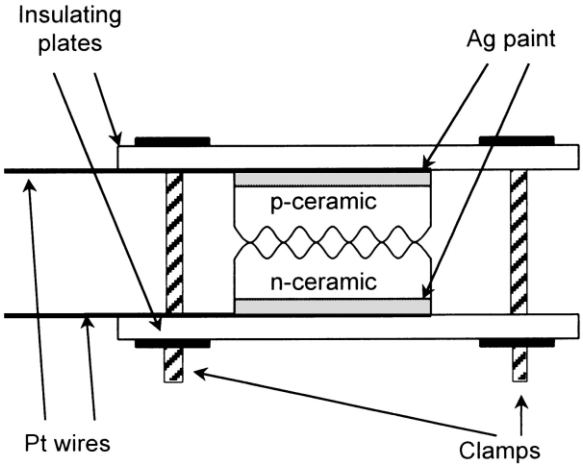

Fig. 1. The sample holder used to assemble the heterojunction sensor.

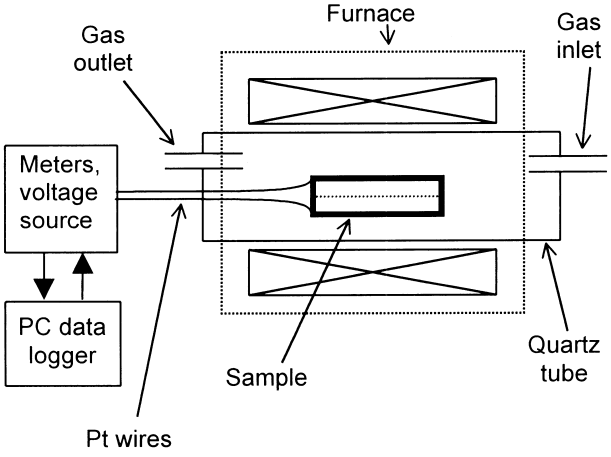

Fig. 2. Schematic diagram showing the controlled atmosphere furnace and metrication system.

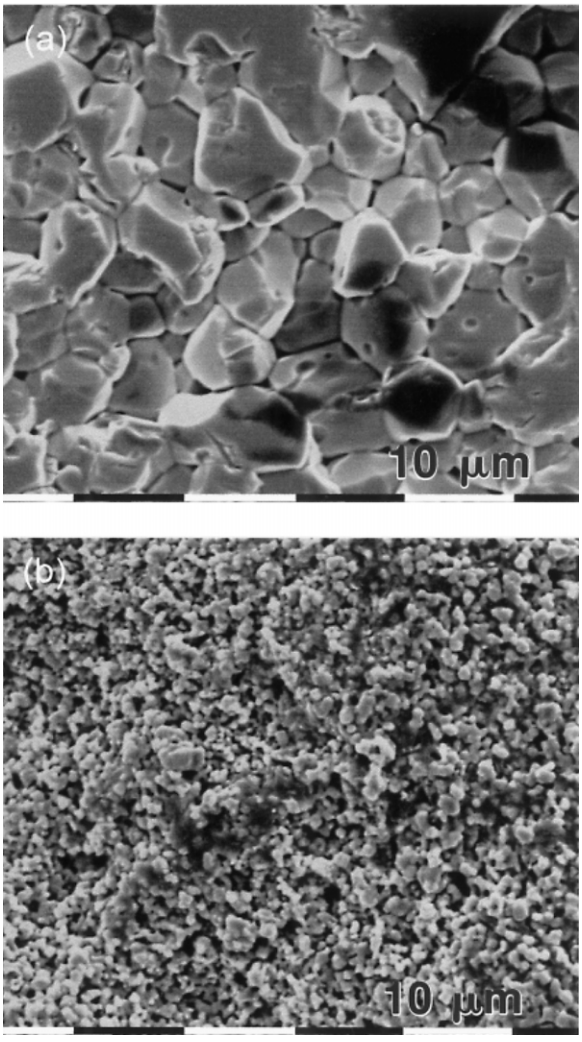

Fig. 3. Secondary electron images of the sensor surfaces. (a) ZnO sensor. (b) $BaTiO_3/CuO/La_2O_3$ sensor. Scale bar = 10 μm.

3.1. ZnO sensor

The ZnO sensor was found to be insensitive to CO_2 in the range 0–2000 ppm, while a small, reproducible increase in resistance was observed when the sensor was exposed to NO_2 (Fig. 4). The response to NO_2 became saturated at concentrations in excess of 4 ppm (Table 1).

3.2. $BaTiO_3/CuO/La_2O_3$ sensor

Sensors with this formulation have previously been reported as showing sensitivity to CO_2 at concentration levels of around 3% using capacitative measurements,[8] although cross sensitivity to NO_2 was not considered. In this study a small reproducible increase in sensor resistance was noted when 1000–5000 ppm CO_2 was introduced. However, this sensor was found to be highly sensitive to NO_2, with a large increase in sensor resistance occurring as the target gas was introduced (Fig. 5). The response time to CO_2 was of the order of 10 min, whilst that to the NO_2 was considerably longer, being around 600 min. The overall sensitivities to CO_2 in the range 0–5000 ppm and NO_2 in the range 0–15 ppm are summarised in Table 1.

3.3. Heterojunction sensor

In order to establish the heterojunction response, a series of I–V measurements were made over a range of applied voltages from + 5 V to −5 V, under different atmospheres.

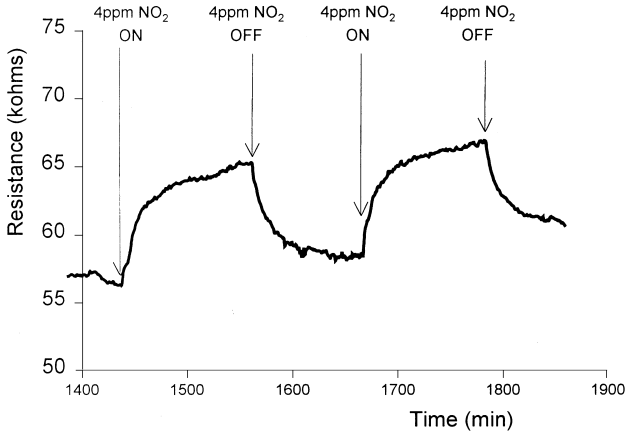

Fig. 4. R–T curve showing the response of the ZnO sensor to 4 ppm NO_2.

Table 1
Sensitivities of the sensors to the target gases

Sensor	CO_2 response (% per 1000 ppm)	NO_2 response (% per 1 ppm)
ZnO	0%	+2.7% (<4 ppm)
		+0.9% (>4 ppm)
$BaTiO_3/CuO/La_2O_3$	+9%	+330%
Heterojunction	0% (<3000 ppm)	−20% (<1.5 ppm)
	−12% (>3000 ppm)	0% (>1.5 ppm)

Fig. 6 shows these. The rectifying nature of the contact formed between the *p*- and the *n*- type ceramics can clearly be seen, although there is a significant reverse bias leakage current.

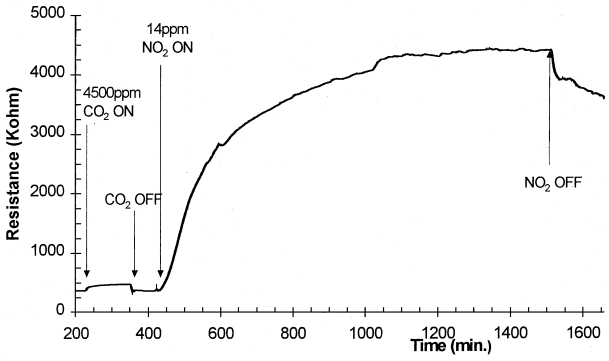

Fig. 5. R–T curve comparing the response of the $BaTiO_3/CuO/La_2O_3$ sensor to 4500 ppm CO_2 and 14 ppm NO_2.

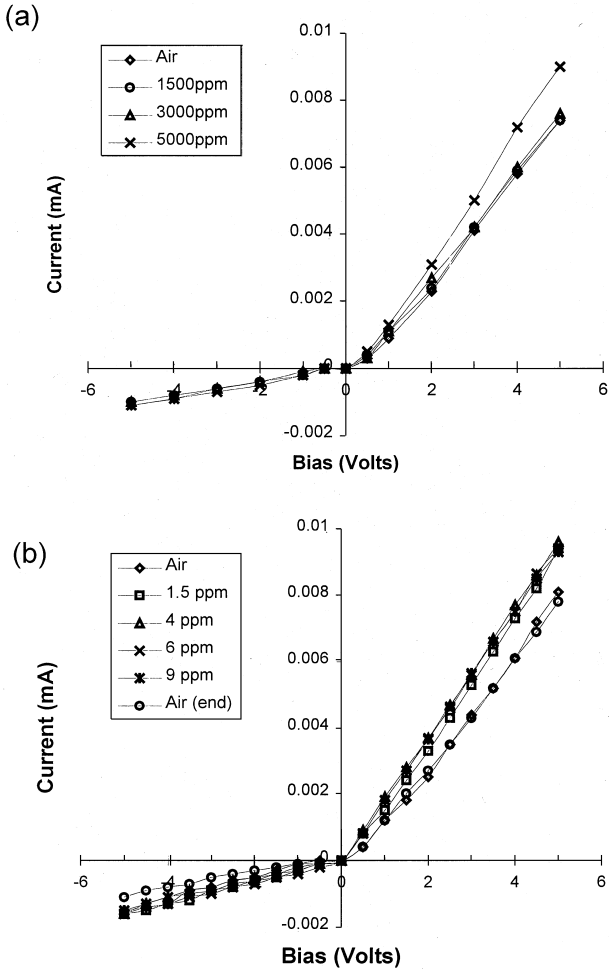

Fig. 6. I–V curves showing the response of the heterojunction sensor to (a) CO_2 and (b) NO_2.

The heterojunction was found to be insensitive to CO_2 in the range 0–3000 ppm, although a small reversible increase was observed in the forward bias current when 5000 ppm CO_2 was introduced [Fig. 6(a)]. When NO_2 was introduced, small reversible increases in both the forward and reverse bias currents were noted. The sensor became saturated after 1.6 ppm of target gas was introduced and further increases in the NO_2 concentration did not affect the measured current.

When a sufficient concentration of either target gas was introduced, there was a corresponding increase in current flow under bias, indicating a decrease in the resistance of the heterojunction. This contrasts with the resistance increases observed for the single pellet sensors and implies a different detection mechanism is active at the heterojunction interface.

Although the overall size of the heterojunction response is small (Table 1), it is distinct from those of the individual sensors, opening the possibility of combining the responses of the individual sensors with that of the heterojunction to improve the overall performance of an inexpensive solid-state gas sensor. Work is currently underway to improve the magnitude of the heterojunction response by preparing an improved structure using thick film techniques.

4. Conclusions

A heterojunction gas sensor was prepared by forming a contact between *n*-type ZnO and a *p*-type $BaTiO_3$/CuO/La_2O_3 composite, and tested in the presence of NO_2 and CO_2 target gases.

Whilst the resistances of the *p*- and *n*-type oxides increased when exposed to the target gases, the resistance of the heterocontact decreased, indicating a different detection mechanism at the heterojunction interface.

The $BaTiO_3$/CuO/La_2O_3 sensor was found to have a high sensitivity to NO_2.

References

1. Nenov, T. and Yordanov, S., *Ceramic Sensors*. Technomic Publishing, Basel, Switzerland, 1996.
2. Yanagida, H., Intelligent ceramics. *Ferroelectrics*, 1990, **102**, 251–257.
3. Hikita, K., Miyayama, M. and Yanagida, H., New approach to selective semiconductor gas sensors using a DC-biased *p–n* heterocontact. *J. Am. Ceram. Soc.*, 1995, **78**, 865–873.
4. Traversa, E., Design of ceramic materials for chemical sensors with novel properties. *J. Am. Ceram. Soc.*, 1995, **78**, 2625–2632.
5. Jung, S. J., Ohsawa, H., Nakamura, Y., Yanagida, H., Hasumik, K. and Okada, O., Effects of Na_2O_3 addition on the gas sensing characteristic of CuO/ZnO heterocontact. *J. Electrochem. Soc.*, 1994, **141**, L53–L55.
6. Jung, S. J. and Yanagida, H., The characterisation of CuO/ZnO heterocontact type gas sensor having selectivity for CO gas. *Sensors and Actuators (B)*, 1996, **37**, 55–60.
7. Traversa, E., Miyayama, M. and Yanagida, H., Gas sensitivity of ZnO/La_2CuO_4 heterocontacts. *Sensors and Actuators (B)*, 1994, **17**, 257–261.
8. Ishihara, T., Kometani, K., Mizuhara, Y. and Takita, Y., A new type of CO_2 gas sensor based on capacitance changes. *Sensors and Actuators (B)*, 1991, **5**, 97–102.