Intelligent gas sensing using an integrated sensor pair

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Abstract

The performance of conductometric gas sensors (e.g. semiconducting oxide) is often reduced by the poisoning of the active film or by poor long-term stability of the output signal. In this paper we propose the use of an integrated pair of sensing elements, one with a narrow electrode gap and the other with a wide electrode gap compared with the film thickness, to recognise or overcome these disadvantages. Equations are derived that describe the steady-state response of such a device for the two limiting cases of a uniform gas concentration within the film (type I) and a distance-dependent one with a boundary (type II). The characteristic response, or operating curve, of a sensor pair for a type I material can then be used as a real-time diagnostic for poisoning of the film, whereas the response for a type II material can be used to improve sensor stability by eliminating undesirable common-mode signals. The basic principles apply to several classes of materials including both organic semiconductors (usually type I) and inorganic semiconductors (usually type II).

Keywords: Gas sensors

1. Introduction

Semiconducting oxide films are commonly used in conductometric gas sensors [1]. Commercial thick-film gas sensors are sold in large numbers by companies such as Figaro Engineering Inc. (Japan) and Capteur Ltd. (UK). However, the application of these sensors as quantitative gas sensors is limited by poor long-term stability due to such effects as poisoning or ageing. This deterioration of performance is clearly of importance if the sensors are to be used to monitor the level of, for example, combustible or toxic gases in air (e.g. CO, NO_x, etc.). Clearly, the performance of this type of sensor can be improved by the development of new poison-resistant materials, however an alternative approach is to exploit the response of a pair of sensing elements rather than a single element [2,3]. In this paper we develop a theory to describe the theoretical response of a pair of sensors and show how the characteristic operating line can be used either to diagnose sensor poisoning or to enhance the stability of semiconducting oxide films which have been doped with catalysts of differing activity.

2. Theoretical response of a pair of sensors

Fig. 1 shows the basic structure of a planar conductometric gas sensor. The principle of operation is to measure the resistance (or conductance) of a film of active material (e.g. doped SnO_2) at an elevated temperature as a target gas is introduced. The thickness of the film depends upon the process technology but is typically in the 1–250 μm region for sintered oxides. Current devices have electrodes of widths that are comparable with or greater than the film thickness and so it is reasonable to assume that the electric field between the electrodes can be approximated by that for a semi-infinite pair of electrodes. However, although the theory that follows can be modified with some effort to cover finite electrode widths [4], interdigital structures
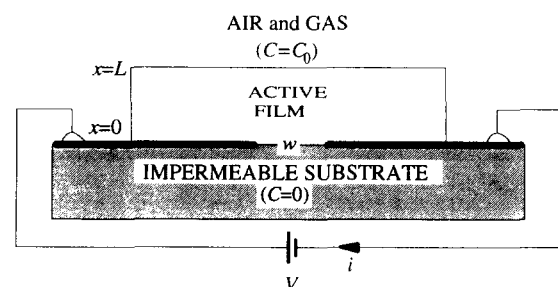

Fig. 1. Basic structure of a conductometric gas sensor.

and indeed finite electrode thicknesses, the fundamental principles are not affected.

The steady-state conductance in air, G_0, of a homogeneous film of conductivity σ_0 and thickness L lying upon semi-infinite electrodes can be found by integrating the current density over a closed surface [5], whence

$$G_0 = \frac{\sigma_0 b}{\pi} \ln\left[\frac{1 + (1 + w^2/L^2)^{1/2}}{w/2L}\right] \tag{1}$$

where w is the separation of the electrodes and b is the length of the electrodes. It is assumed that the edge effects can be neglected (i.e. $b \gg w$).

When a gas of concentration C_0 is introduced it can diffuse into the porous film and react at sites (e.g. at grain boundaries) dispersed uniformly throughout the film. These reaction sites modify the local conductivity of the film according to some function that depends upon the local gas concentration C_x. The concentration dependence of the local conductivity $\sigma(C_x)$ may be related to a response function $F(C_x)$ via

$$\sigma(C_x) = \sigma_0[1 + F(C_x)] \tag{2}$$

The exact form of the response function is governed by the chemical reaction taking place in the film and two limiting examples are evaluated below.

Eq. (2) can now be used to calculate the steady-state response $\mathscr{R}$ (i.e. fractional change in conductance) of the sensor by integrating the concentration-dependent current density:

$$\mathscr{R} = \frac{G(C_x) - G_0}{G_0} = \frac{\sigma(C_x) - \sigma_0}{\sigma_0}$$

$$= \frac{\displaystyle\int_{x/L=0}^{x/L=1} F(C_x)/[(x/L)^2 + (w/2L)^2]^{1/2} \, \mathrm{d}(x/L)}{\ln\{[1 + (1 + w^2/4L^2)^{1/2}]/(w/2L)\}} \tag{3}$$

Two advantages of expressing the response as the fractional change in conductance are that it becomes independent of the electrode length b and it is directly proportional to the concentration-dependent function $F(C_x)$.

Now let us consider the response of a pair of sensing electrodes, one with an electrode gap w_n that is narrow compared with the film thickness (i.e. $w_n \ll L$) and the other with an electrode gap w_w that is wide compared with the film thickness (i.e. $w_w \gg L$). In the case of the narrow-gap sensor, nearly all the electric field is effectively enclosed within the film and so the baseline conductance G_{0n} given by Eq. (1) simplifies to

$$G_{0n} \approx \frac{\sigma_0 b}{\pi} \ln\left(\frac{4L}{w_n}\right) \quad \text{where} \quad \frac{w_n}{L} \ll 1 \tag{4}$$

and so from Eqs. (3) and (4) the response of the narrow-gap sensor becomes

$$\mathscr{R}_n \approx \frac{\displaystyle\int_{x/L=0}^{x/L=1} F(C_x)/[(x/L)^2 + (w_n/2L)^2]^{1/2} \, \mathrm{d}(x/L)}{\ln(4L/w_n)} \tag{5}$$

In the case of the wide-gap sensor, the base-line conductance G_{0w} can be simplified by using the first term in a Maclaurin expansion of the log to give

$$G_{0w} \approx \frac{2}{\pi} \frac{\sigma_0 bL}{w_w} \tag{6}$$

In effect, the sensing electrodes now behave like a parallel-plate structure (except the prefactor is $2/\pi$ rather than unity). As the electric field inside the film is nearly constant and independent of the distance x, Eq. (3) can be reduced to

$$\mathscr{R}_w \approx \int_{x/L=0}^{x/L=1} F(C_x) \, \mathrm{d}(x/L) \tag{7}$$

where the response of the wide-gap sensor is independent of the electrode separation (as well as the electrode length).

We can now consider the response of a pair of sensing elements lying under the same film, as shown in Fig. 2, in which one electrode separation is small ($w_n/L \ll 1$) and the other is large ($w_w/L \gg 1$). The output of each sensor of the sensor pair ($\mathscr{R}_n$, $\mathscr{R}_w$) can be seen in the two-dimensional plot of the response of the narrow-gap sensor against that of the wide-gap sensor. We are interested in the steady-state output from the sensor pair and we will define it as the ratio of the individual sensor responses, which is just the gradient (through the origin) of the two-dimensional plot. For semi-infinite electrodes, we obtain

$$\frac{\mathscr{R}_n}{\mathscr{R}_w} \approx \frac{\displaystyle\int_{x/L=0}^{x/L=1} F(C_x)/[(x/L)^2 + (w_n/2L)^2]^{1/2} \, \mathrm{d}(x/L)}{\ln(4L/w_n) \displaystyle\int_{x/L=0}^{x/L=1} F(C_x) \, \mathrm{d}(x/L)} \tag{8}$$

As we shall see, this response ratio is a useful parameter because it depends upon the non-uniformity of the gas concentration profile within the film via $F(C_x)$.
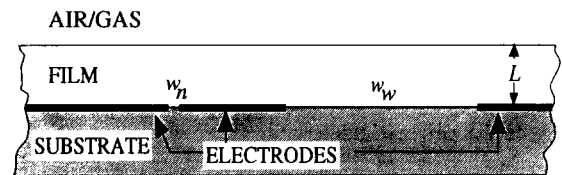

Fig. 2. Structure of an integrated pair of conductometric gas sensors, one with a narrow electrode gap ($w_n \ll L$) and the other with a wide electrode gap ($w_w \gg L$) compared with the film thickness.

We will now consider the effect of two profiles, which illustrate the limiting cases, on the characteristic behaviour of the sensor pair and then discuss their practical significance.

3. Results

3.1. Uniform gas profile (type I)

The simplest gas profile to occur would be one in which the steady-state gas concentration inside the film is a constant and so independent of the distance x, as shown in Fig. 3. In this case (type I), the response function $F(C_x)$ is simply related to the external gas concentration C_0, i.e.

$$F(C_x) = F_1(C_0) \tag{9}$$

Type I behaviour can be expected in (a) polymer films and (b) semiconducting oxides with a low concentration of reaction sites.

(a) In polymer films an adsorption/desorption process controls the conductance changes. For example, it has been observed that a Langmuir adsorption isotherm can describe the response of conducting polymers [6],

$$F_1(C_0) = k_1 \frac{KC_0}{1 + KC_0} \quad \text{or} \quad k_1 KC_0 \quad \text{when} \quad KC_0 \ll 1$$

$$\tag{10}$$

where K is a reaction-rate coefficient (and can include a partition coefficient if necessary) and k_1 is a parameter that depends upon the sensitivity of the material to a particular gas. This becomes a linear response function at low gas concentrations, and this behaviour has been observed.

(b) In the case of semiconducting oxides, there is an irreversible combustion process taking place within the film rather than a reversible sorption process [7]. However, if there are relatively few reaction sites within the film and/or their reaction rate is low (i.e. a low

catalytic activity of dopant in the oxide), then a negligible amount of the gas entering the film will be consumed and so the gas profile will be uniform. Under these conditions, the steady-state response function is given by the well-known power law

$$F_1(C_0) = k_2 C_0^n \quad \text{where} \quad 0 < n < 1 \tag{11}$$

where k_2 is the gas-sensitivity parameter for a semiconducting oxide material and the exponent n normally lies between 0.3 and 0.9.

The steady-state response of this type of sensor pair is straightforward as the concentration profile (from Eq. (11)) is independent of distance x and so the geometric factors in Eq. (8) must cancel out to leave $F_1 = \mathcal{R}_n = \mathcal{R}_w$. The two-dimensional plot becomes a straight line as shown in Fig. 4. As the concentration increases, so the length of the response vector $(\mathcal{R}_n^2 + \mathcal{R}_w^2)^{1/2}$ increases. When the response is linearly related to gas concentration, the length of the vector scales linearly whereas for non-linear behaviour its rate of increase slows down (e.g. see Eq. (11) with $n < 1$), or, in the case of the Langmuir isotherm, has a maximum value of $\sqrt{2}k_1$ (from Eq. (10)).

The sensor pair response vector will always lie upon the line, even during the time to reach equilibrium — unless the process is diffusion-rate limited so that the response of the narrow-gap sensor lags behind that of the wide-gap sensor (e.g. see case I of Ref. [8]). Thus the line represents the characteristic behaviour of the sensor pair and $\mathcal{R}_n/\mathcal{R}_w$ should have a value of unity during the lifetime of the sensors.

The presence of an interfering gas will not move the response vector off the characteristic operating line because it will affect both sensors equally (unless its concentration profile is not uniform like the target gas). However, if the outside part of the film is poisoned at some time during the lifetime of the sensor pair
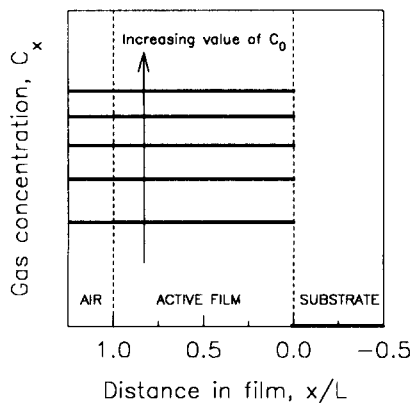

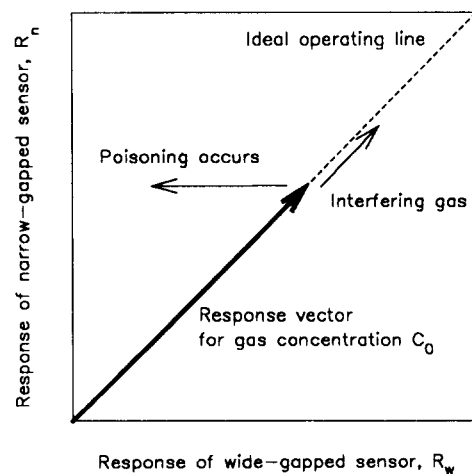Fig. 3. Uniform gas profile in the active film (type I).

Fig. 4. Theoretical response of the sensor pair to a gas with a type I concentration profile (uniform) with arbitrary units.

then the response of the wide-gap sensor will fall while the response of the narrow-gap sensor will remain unchanged. Consequently, the pair response parameter $\mathscr{R}_n/\mathscr{R}_w$ will fall below unity as the oxide (or polymer) film poisons and acts as a diagnostic tool (see Fig. 4). A simple real-time method of obtaining the pair response parameter would be to use an analogue electronic circuit to compute the response ratio. Any deviation of the resistance ratio from unity could then trigger an alarm. However, if the poisoning effect is evenly distributed throughout the film then the response vector will not move off the characteristic operating line but simply reduce its length. This behaviour could only be detected by the frequent use of a calibration gas.

3.2. Moving-boundary gas profile (type II)

When a semiconducting oxide material is doped with a catalyst of high activity, it is probable that the gas entering the film is rapidly consumed and so does not penetrate all the way into the film, which is the converse of a type I profile. The simplest model would be to have a boundary set up under steady-state conditions, as sketched in Fig. 5, which divides the gas-penetrated from the unpenetrated parts of the film. Then, the boundary moves into the film as the surface gas concentration is increased until it reaches the impermeable substrate. At this stage and at higher concentrations the gas concentration within the film becomes uniform. The response function can now be written as

$$F_{II}(C_x) = \begin{cases} k_2 C_0{}^n & x_b \leqslant x \leqslant L \\ 0 & 0 \leqslant x < x_b \end{cases} \qquad (12)$$

The response of the wide-gap sensor now becomes simply the fraction of the film penetrated by the gas multiplied by the isotherm, hence

$$\mathscr{R}_w \approx k_2 C_0{}^n \int_{x_b/L}^{1} \mathrm{d}(x/L) = k_2 C_0{}^n (1 - x_b/L) \qquad (13)$$
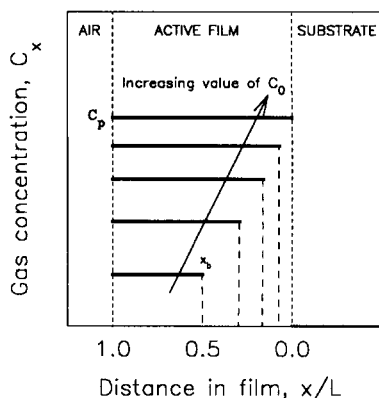

Fig. 5. Moving-boundary gas profile in an active film (type II).

The response of the narrow-gap sensor can also be found from Eqs. (7) and (12) for this profile where

$$\mathscr{R}_n = k_2 C_0{}^n \frac{\ln\left[\dfrac{1 + (1 + w_n{}^2/4L^2)^{1/2}}{x_b/L + (x_b{}^2/L^2 + w_n{}^2/4L^2)^{1/2}}\right]}{\ln\left[\dfrac{1 + (1 + w_n{}^2/4L^2)^{1/2}}{w_n/2L}\right]}$$

$$\approx k_2 C_0{}^n \frac{\ln\{2/[x_b/L + (x_b{}^2/L^2 + w_n{}^2/4L^2)^{1/2}]\}}{\ln(4L/w_n)} \qquad (14)$$

Substituting this into Eq. (8) gives the response of the sensor pair, which is now a function of the position of the boundary, i.e., when $x_b = 0$,

$$\frac{\mathscr{R}_n}{\mathscr{R}_w} \approx \frac{\ln\{2/[x_b/L + (x_b{}^2/L^2 + w_n{}^2/4L^2)^{1/2}]\}}{\ln(4L/w_n)(1 - x_b/L)} = 1 \qquad (15)$$

As discussed above, the boundary moves into the film as a function of the external gas concentration C_0 until at a certain concentration C_p the boundary meets the inside of the film and the profile becomes uniform again (i.e. type I). The value of the penetration concentration will depend upon parameters such as the catalytic activity of the dopant and the density of the reaction sites. From the study of diffusion-reaction phenomena [9], it is reasonable to assume that the moving boundary follows a fractional power law,

$$\frac{x_b}{L} = 1 - \left(\frac{C_0}{C_p}\right)^m \qquad (16)$$

where the exponent m is likely to be about 0.5, since it becomes increasingly difficult to move the internal boundary with increasing concentration.

Fig. 6 shows the operating characteristic for this type of profile calculated from Eqs. (15) and (16) where both the conductance and boundary exponents n and m are set to a value of 0.5, and k_2 is set to unity. In region A $(C_0 < C_p)$, the gas does not penetrate far enough into the film to reach all of the field lines of the narrow-gap electrodes and so the sensor provides a reduced response. The deviation from the type I operating curve depends upon the value of the narrow electrode gap, as shown in Fig. 6. Once again, poisoning of the film will be apparent as the operating line shifts, only it will be more dramatic as the unreacted gas begins to reach the inner electrodes, turning the narrow-gap sensor hard on as the wide-gap sensor is turned partly off. It should be noted that an intelligent choice of the electrode separation could ensure that the narrow-gap sensor turns on at a particular gas concentration and thus provide an alarm level that is less prone to drift. In region B $(C_0 > C_p)$, the sensor pair behaves exactly as in the case of a type I profile and the characteristic operating line has unit slope.
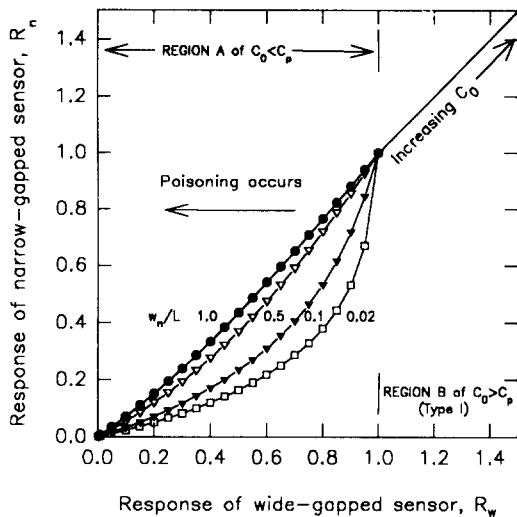
Fig. 6. Theoretical responses of an integrated sensor pair to a gas with a type II concentration profile (moving boundary) at various narrow electrode gaps w_n/L of 1.0, 0.5, 0.1, and 0.02. The wide electrode gap w_w/L is fixed at a value of 10 and the gas-sensitivity constant k_2 is set to unity.
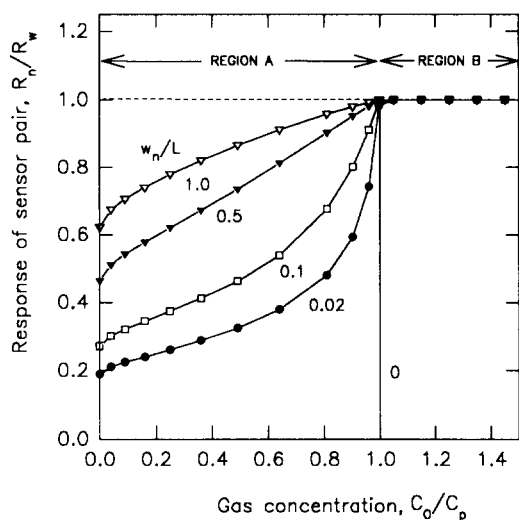

Fig. 7. Theoretical concentration response of a type II integrated sensor pair parameter against the external gas concentration (relative to the penetration gas concentration) with various narrow electrode gaps w_n/L of 1.0, 0.5, 0.1, and 0.02. The wide electrode gap w_w/L is fixed at a value of 10.

Fig. 7 shows the variation of the sensor pair parameter $\mathscr{R}_n/\mathscr{R}_w$ as a function of the external gas concentration (relative to the penetration gas concentration C_p). The same values of m, n, k_2 and w_n/L have been used as in Fig. 6. For films doped with highly active catalysts, the penetration depth is very small and so the operating curve stays in region A close to the origin, especially where the electrode gap tends to zero, since the profile tends to a step function at the penetration gas concentration C_p. In this region the sensor pair response ratio can be used but with a different functionality than before. Now the narrow-gap sensor is less dependent

on the external gas concentration (i.e. when w_n/L is small) but shows a step change near C_p and so may be used as a concentration detector. The narrow-gap sensor now compensates for any common-mode variation in film properties, e.g. a temperature fluctuation, change in reaction-rate constant or a gas-independent ageing process. The principle is similar to that of a silicon thermotransistor which uses the collector-current ratio (see Ref. [1], p. 105).

4. Conclusions

Expressions have been derived which define the response of a pair of planar conductometric gas sensors. The combination of a narrow-gap sensor and a wide-gap sensor leads to some useful properties of the sensor pair such as providing a simple diagnostic signal or enhanced stability. The realisation of such a device is possible using current material processing technology. Thus, in the application of thick active films of about 100 μm the narrow electrode gap should be about 10 μm and it can be made by using conventional UV lithography (e.g. phthalocyanines [10]), whereas in the application of thin active films of about 1 μm the narrow electrode gap of 0.1 μm can be micromachined using focused ion beam milling [11]. The integration of the sensor pair on the same substrate and under the same active layer means that the process variability is minimised, which is a useful advantage in manufacture.

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Biography

Julian W. Gardner graduated from Birmingham University in 1979 with a first class honours degree and then studied the properties of thin films at the Cavendish Laboratory for his Ph.D. From 1983 to 1987 he worked first at AEA Technology Ltd. and later at Molins Advanced Technology Unit on instrumentation. At Molins he developed a novel opto-electronic sensor that has been packaged in the UK and US for implementation on high-speed packaging machinery. Since joining Warwick University as a lecturer in 1987, his research interests have been sensor materials, the design of integrated gas array sensors and electronic noses. In 1989 he received the Esso Centenary Education Award sponsored by the Royal Society and a Fellowship of Engineering to pursue his research interests. He was Director of a NATO advanced research workshop on electronic noses in 1991 and has published over 80 technical papers and three books. In 1992 he became a Senior Lecturer at Warwick University and has recently been awarded an Alexander von Humboldt Fellowship in Germany. He is now the Director of the Sensors Research Laboratory in the Centre for Nanotechnology and Microengineering at Warwick University.