Effect of Electrode Geometry on Sensor Response

UMA JAIN*, A. H. HARKER and A. M. STONEHAM

Theoretical Physics Division, Harwell Laboratory, Didcot, Oxon, OX11 0RA (U.K.)

D. E. WILLIAMS

Materials Development Division, Harwell Laboratory, Didcot, Oxon, OX11 0RA (U.K.)

Abstract

We have demonstrated the feasibility of using a finite-element program to study the effect of electrode geometry on the performance of an oxide gas sensor. The gas concentration is varied within the sensor. The program is general enough to be extended to complex three-dimensional geometries. For the simpler cases we consider, we find that at a given temperature the back contact sensor will be more selective for moderately reactive gases than for less or more reactive ones, which is in general agreement with the observations made on Figaro gas sensors. We also find that the performance of the sensor improves by using interlacing electrodes, as expected.

Introduction

Gas sensors based on semiconducting oxide are used for the detection of combustible and noxious gases in air. The general mechanism of semiconductor gas sensor operation has been widely described in the literature [1–8].

In a separate paper [9], we discussed the effect of temperature and gas concentration on sensor response when the conductance of the sensor varies along the direction of diffusion of the gas. We considered the case of one-dimensional diffusion with the electrodes positioned on the vertical ends of a horizontal slab, into which gas was allowed to diffuse from above. We divided the sensor into layers perpendicular to the direction of diffusion. The conductance of the sensor was then simply the sum of the conductances of each layer.

In general, however, the electrodes will not be positioned in such a simple way. Also, we expect the position of the electrodes to affect the conductance of the sensor and hence its response, significantly.

In order to study the effect of electrode geometry on the conductance of a sensor, four different confi-

gurations were considered. The cross section of the sensor is in the $X–Y$ plane and it is assumed that the electrodes extend infinitely along the Z axis.

Sensor Geometry and the Numerical Model

Figure 1 illustrates the four different configurations. The $X–Y$ plane under consideration is divided into square elements and the finite-element program TGSL [10], developed in the Theoretical Physics Division, Harwell, is used to solve for the electrostatic potential V from eqns. (1) and (2) below.

In the steady state

$$\mathrm{div}\, \boldsymbol{J} = 0 \tag{1}$$

where $\boldsymbol{J}$ is the current flux

$$\boldsymbol{J} = -(1/\rho)\, \nabla V \tag{2}$$

ρ is the resistivity and V is the potential. The electric current passing through the surfaces of the sensor, other than the electrodes, is set equal to zero.
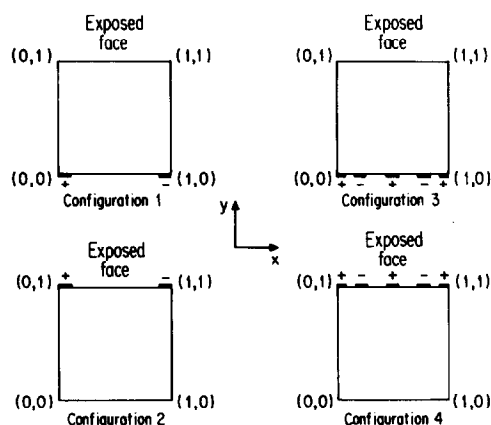

Fig. 1. The four electrode geometries considered in the present work. The positions of the electrode are as follows. Configuration 1: anode {(0, 0)–(0.1, 0)}; cathode {(0.9, 0)–(1.0, 0)}. Configuration 2: anode {(0, 1)–(0.1, 1)}; cathode {(0.9, 1)–(1, 1)}. Configuration 3: anode {(0, 0)–(0.05, 0), (0.45, 0)–(0.55, 0), (0.95, 0)–(1, 0)}; cathode {(0.15, 0)–(0.25, 0), (0.75, 0)–(0.85, 0)}. Configuration 4: anode {(0, 1)–(0.05, 1), (0.45, 1)–(0.55, 1), (0.95, 1)–(1, 1)}; cathode {(0.15, 1)–(0.25, 1), (0.75, 1)–(0.85, 1)}.

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*Present address: Department of Materials Science and Engineering, MIT, Cambridge, MA 02139, U.S.A.,
Permanent address: Gargi College, University of Delhi, India.

The functional dependence of the resistivity on gas concentration is taken to have the usual form [11],

$$\rho = \rho_0(1 + KP_1)^{-\beta} \tag{3}$$

where K depends on the rate constant of the reaction of the reducing gas with oxygen and P_1 is the partial pressure of the reducing gas. The exponent β, which depends on the temperature and a characteristic energy of the surface [11], is given a range of values from 0.2 to 0.5 or higher [12].

The concentration c of the reducing gas is a function of y, the direction of diffusion of the gas, and $y = 1$ is the face exposed to the reducing gas. c satisfies the diffusion equation [13]

$$\partial c/\partial t = D\partial^2 c/\partial y^2 - K_1 c \tag{4}$$

where D is the diffusion constant of the reducing gas and K_1 is related to the rate constant of the reaction of the reducing gas and oxygen. The concentration of oxygen is assumed to be constant.

In the steady state

$$\partial c/\partial t = 0 \tag{5}$$

and the solution of eqn. (4) under the boundary condition

$$c = 1 \text{ at } y = 1 \tag{6}$$

for the front surface which is exposed to the gas and the boundary condition

$$\partial c/\partial y = 0 \text{ at } y = 0 \tag{7}$$

for the back surface is

$$c(y) = \cosh(y\sqrt{K'})/\cosh(\sqrt{K'}) \tag{8}$$

where

$$K' = K_1/D \tag{9}$$

The resistivity ρ as a function of y is, therefore,

$$\rho(y) = \rho_0[1 + KP_1 \cosh(y\sqrt{K'})/\cosh(\sqrt{K'})]^{-\beta} \tag{10}$$

This simplified formulation is used in order to have an analytical expression for $\rho(y)$. However, the program can be easily modified to compute ρ numerically for different values of y. We used the TGSL finite-element subroutine library [10], adding subroutines to define eqns. (1) and (2) and to define $\rho(x, y)$. We calculated the current flows by integrating over eqn. (2). The four electrode configurations considered are shown in Fig. 1.

Results and Discussion

Figures 2(a) and (b) show the current (in arbitrary units) as a function of gas concentration for the four different cases. For want of data on values of rate constants, we have made simplified calculations using $K = K'$. Since the purpose is to test the effect of elec-
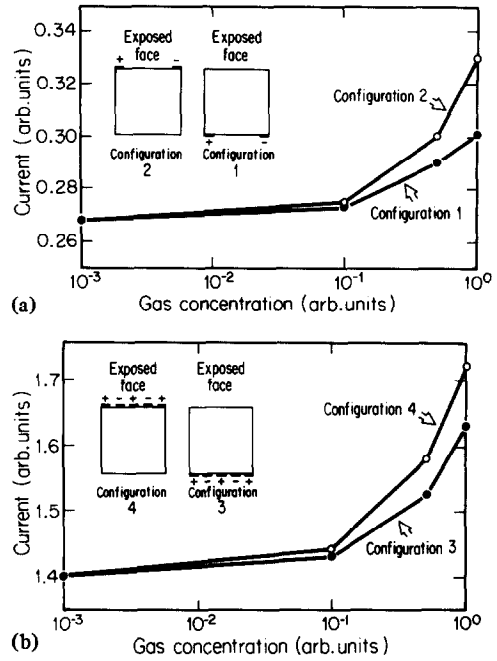

Fig. 2. (a) The current (in arbitrary units) as a function of gas concentration for configurations 1 and 2. $\beta = 0.3$, $K = K' = 1$. Partial pressure of O_2 is 1. (b) Same as (a), but for configurations 3 and 4.

trode geometry, representative values of K are chosen: we have used 1, 10 and 100. It is clear from eqn. (3) that for concentrations large enough so that the product of the rate constant K and the gas concentration P_1 is comparable to one, the current output increases rapidly with gas concentration. This is clearly evident from all the four curves in Figs. 2(a) and (b). The magnitude of the current is much larger for configurations 3 and 4, as is to be expected.

Figures 3, 4, 5 and 6 show the effect of increasing the rate constant K for the four different configurations. The dependencies on K shown in Figs. 3 and 5 are markedly different from those in Figs. 4 and 6. In Figs. 3 and 5 (which are for configurations 1 and 3 where the electrodes are on the unexposed surface) the current increases as K is increased from 1 to 10
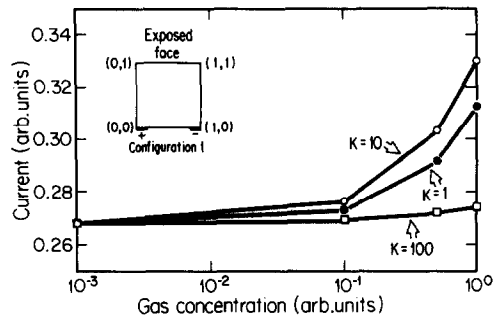

Fig. 3. The current (in arbitrary units) as a function of gas concentration for configuration 1 for three different values of $K(= K')$.
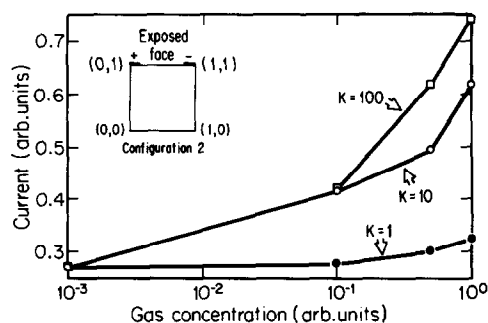
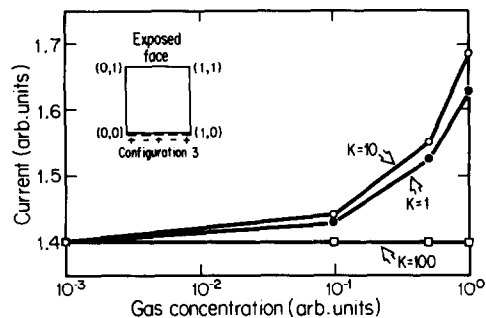Fig. 4. Same as Fig. 3 for configuration 2.

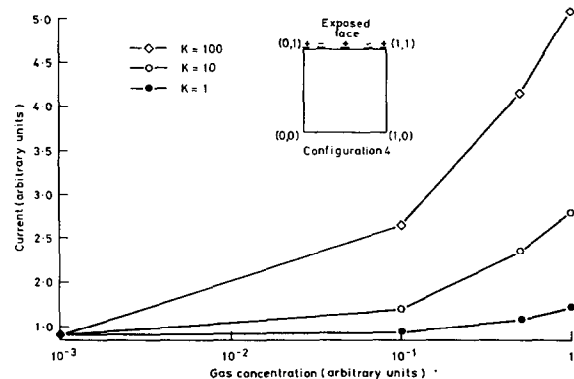Fig. 5. Same as Fig. 3 for configuration 3.

Fig. 6. Same as Fig. 3 for configuration 4.

and then decreases and remains almost constant with gas concentration as K is increased to 100. In Figs. 4 and 6 (which are for configurations 2 and 4 where the electrodes are on the exposed surface) the rate of increase in current with gas concentration increases continuously as K is increased from 1 to 100.

This difference in behaviour can be explained as follows. As the rate constant K increases, two effects take place simultaneously. First, as K increases, more and more absorbed O_2 molecules combine with the absorbed molecules of the reducing gas. Thus fewer electrons are captured by these molecules, and hence the resistance decreases. This is clear from eqn. (3), where the term KP_1 increases with increasing K.

However, at the same time the concentration of the reducing gas itself decreases as K_1 increases, as is clear from eqn. (4). This decrease is significant for planes close to $y = 0$, but not near the plane $y = 1$ where the concentration is almost equal to unity. As a result, the resistivity near the plane $y = 0$ increases with increasing K, but not the resistivity near the plane $y = 1$.

As a result of these two opposing effects, for the electrodes situated on the plane $y = 1$ the current will increase with increasing K, whereas for electrodes on the plane $y = 0$ the current will at first increase then decrease with increasing K.

It is clear from the above discussion that for sensors with electrodes on the plane $y = 0$, i.e., for back contact sensors, a plot of conductance versus K will show a peak. A peak in response to variation in K can be considered a peak in temperature response, since K is a function of temperature. Such conductance temperature peaks are often observed for tin oxide gas sensors [4, 5, 14]. However, since our aim in this paper is to emphasize the effect of electrode geometry, we have considered only a few representative values of K and have not taken into account explicitly the dependence of the rate constant and the diffusion constant on temperatures. It would, therefore, be hard to make a definite statement on the variation of conductance with temperature from these figures.

For sensors with electrodes on the plane $y = 1$, i.e., for front contact sensors, there is no conductance peak with variations in K, a result consistent with speculation in the recent sensor literature.

The above results also lead us to expect that different types of reducing gases will show conductance peaks at different temperatures. This also means that at a given temperature, the back contact sensor will be more selective for moderately reactive gases than for less or more reactive ones. Some Figaro gas sensors seem to work this way. A front contact sensor will not show such selectivity, but will produce a higher current output.

We also note that the magnitude of the current output is much larger for interlacing electrodes (configurations 3 and 4), as is obviously expected.

Conclusions

The present work clearly demonstrates the feasibility of using a finite-element program to study the effect of electrode geometry on sensor response. The advantages of this method are obvious. It is possible to study the effect of electrode configurations more complicated than the ones we have considered here and for which obvious qualitative conclusions cannot be drawn. Also, since K and therefore ρ can be varied from element to element, it is possible to study the effect of surface inhomogeneities or catalysts.

The finite-element program used can be extended to three-dimensional cases, so the effect of asymmetrical electrode geometries can also be considered.

Acknowledgement

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Biographies

Uma Jain received her B.Sc.(Hons.) physics and M.Sc. physics degrees at the University of Delhi, India. She carried out her doctoral research on radiation damage in alkali halides at the Atomic Energy Research Establishment, Harwell, U.K. and received her Ph.D. degree from the Indian Institute of Technology, Delhi. She is a senior lecturer at Gargi College, University of Delhi and is currently visiting at the Department of Materials Science and Engineering, M.I.T., U.S.A., working on a theoretical model for the metamict transformation in irradiated silica.

Anthony Harker, D.Phil., F. Inst. P., is a group leader in the Theoretical Physics Division of the United Kingdom Atomic Energy Authority's Harwell Laboratory. His research career has been at Harwell (except for a Fellowship at the Technische Hochschule, Stuttgart) and has been devoted to solid-state physics, non-destructive testing, and the modelling of physical processes. He has published many research papers and a book on *Elastic Waves in Solids.*

Marshall Stoneham, Ph.D. F. Inst. P., F.R.S., is the head of the Materials Physics and Metallurgy Division at the United Kingdom Atomic Energy Authority's Harwell Laboratory. He has been a visiting professor at the Universities of Illinois, Connecticut and Keele. As well as his extensive publication of research papers, he has written a book on the *Theory of Defects in Solids,* and is co-author of two more. He is on the editorial board of several learned journals. His reserach interest began with solid-state physics, but spread out to cover a wide range of physics and applied science.

David Williams is currently leader of the Sensors Group in the Materials Development Division at Harwell, and visiting professor in chemistry at Southampton University. He graduated in chemistry from the University of Auckland, New Zealand, and obtained his Ph.D. there in 1974, for studies on the electrochemistry and photoelectrochemistry of thin anodic oxide films on metals. He joined Harwell in 1980, after postdocotral research at Oxford and Imperial College, and industrial research experience at IMI Titanium. His research interests include semiconducting oxide devices for gas concentration measurement, electroanalytical methods and the electrochemistry of corrosion processes, which includes the development of scanning laser methods for imaging surface chemistry.