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Gas sensing properties of the mixed molybdenum tungsten oxide, $W_{0.9}Mo_{0.1}O_3$†

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The mixed oxide $W_{0.9}Mo_{0.1}O_3$ responds sensitively to oxidizing gases such as ozone and NOx in air and suffers only a mild interference from changes in relative humidity. The mixed oxide has a small activation energy for conduction (0.1 eV) and an unusual concentration dependence of response at low temperatures. Possible response mechanisms are considered.

1. Introduction

The notion of employing semiconducting oxides in gas sensors was first proposed almost 40 years ago.[1] Since the first observation of high sensitivity to the presence of impurity gases in an air ambient there have been a huge number of reports describing the gas sensing behaviour of tin oxide and this work was comprehensively reviewed in 1995.[2] The surface reaction controlling the responses of semiconducting oxides to reducing gases in air at temperatures in the range 300–500 °C is believed to involve changes in the concentration of surface oxygen species such as O^{2-}. The formation of such ions by oxygen adsorbed at the gas–solid interface abstracts electrons from the bulk of the solid; the oxygen can thus be thought of as a trap for electrons from the bulk. In the presence of a reducing gas such as carbon monoxide, a surface catalyzed combustion

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (1)$$

may take place so that the surface coverage of adsorbed oxygen ions may be decreased and the resistance decreased as a consequence of the reduction in both the surface potential and the depletion depth.[3] In support of this mechanism it has been observed that carbon monoxide undergoes combustion on the surface of tin oxide at temperatures above 300 °C.[4]

It has also been found that semiconducting oxide sensors can respond very sensitively to the presence of oxidizing gases in a background of air[5,6] but much less is known about the mechanisms involved in the reactions with oxidizing gases than about those involved in the reactions with reducing gases. Certainly it is not possible that a combustion-like reaction such as is represented by eqn. (1) could be responsible for such responses.

Tin oxide gas sensors respond sensitively to changes in relative humidity[7] and this moisture response represents a severe limitation on the utility of tin oxide gas sensors. The possibility that this response, too, arises from a different mechanism from that involved in detecting reducing gases suggests that it should be possible to achieve a selective response to extraneous gases in air without interference from changes in relative humidity. The search for a selective response involves a consideration of alternative semiconducting oxides and different operating temperatures. Recently some semiconducting materials have been reported with a very favourable ratio of response to gas compared to response to humidity. These include $Cr_{2-x}Ti_xO_{3+z}$,[8] cadmium germanium oxynitride[9] and MO_{3-x}, where M is predominantly molybdenum but can contain a small amount of a 5-valent ion.[10]

Clearly a variety of patterns of gas sensing properties can be expected amongst the large number of semiconducting materials known.[6] The fundamental properties of pure oxides can be modified to provide further diversity by doping methods, although such techniques must be managed with great care in order to avoid unwanted segregation of second phases. It is the composition of the oxide surface, that dictates the properties of a semiconductor gas sensor. If the particle size of the oxide is 0.1 microns and the particles are equi-axed (approximately of cubic shape), then a simple calculation shows that a mono-layer surface coverage of a "foreign" oxide can be achieved with an "impurity" concentration of 0.01 mole %.

By way of example, it has been reported that a surface covering of only one tenth of a mono-layer of silver oxide is sufficient to alter the sensing characteristics of tin oxide to more resemble those of silver oxide than of the substrate (tin oxide).[4] Following such considerations, a patent[11] describing the ozone detection characteristics of a WO_3 sensor teaches that the sensor material must be at least 99% pure.

The present paper describes the gas sensing properties of the mixed molybdenum tungsten oxide, $W_{0.9}Mo_{0.1}O_3$, which serves to extend the variety of behaviour exhibited by semiconductor gas sensor materials.

2. Experimental

The mixed molybdenum tungsten oxide was prepared following a method described in the literature:[12]

48 grams of $(NH_4)_6W_7O_{24}\cdot 6H_2O$ (Aldrich 32,238–5, 99.99%) and 5 grams of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich 27,790–8, 99.98%) were dissolved in 500 ml of hot distilled water. The

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†Electronic supplementary information (ESI) available: A. Scanning electron micrograph of the surface of a mixed molybdenum tungsten oxide gas sensor revealing an open structure and a particle size range from 0.1 to 5 microns. B. Elemental analysis (by X-ray wavelength) of the mixed molybdenum tungsten oxide prepared and used in this study. C. Responses of a mixed molybdenum tungsten oxide sensor at two temperatures to the introduction of 1% methane into an atmosphere of dry air. See http://www.rsc.org/suppdata/jm/b1/b111118n/

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mixed solution was evaporated to dryness over a period of 3 hours. The dried powder was heated in a closed furnace to 700 °C for 2 hours. The powder was dispersed in an organic vehicle and screen printed over gold interdigitated electrodes on an alumina substrate to give an oxide layer thickness of approximately 50 microns. The tiles, which had previously been equipped with a platinum resistance heater printed on the reverse, were fired at 700 °C for 1/2 hour. Scanning electron microscopy showed that the oxide layer has a very open structure with a broad range of particle sizes between approximately 0.1 and 5 microns. Wavelength-dispersive analysis of X-rays from the surface of the sensor showed only peaks from tungsten, molybdenum and oxygen.

For gas response tests, a certified stock supply of 20 ppm NO in nitrogen (Air Liquide) was mixed, *via* a system of mass flow controllers, with air. NO reacts with oxygen spontaneously to form NO_2,[13] but the indirect origin of the NO_2 used here is acknowledged by the use of the label "NOx" in the presentation of the results. This is a widely used convention.[13,14] The sensors respond to the NOx test gas with a resistance increase (conductance decrease). This characteristic of an oxidizing gas is also displayed when the sensors are exposed to ozone, see below. NO is so readily oxidized that, if it were to be sensed before it could react with air to form NO_2, it should behave as a reducing gas and provide a resistance decrease on an n-type semiconductor.

Ozone was supplied from a transfer standard reference source supplied by N.I.S.T. in the laboratory of the Environmental Protection Agency, Research Triangle Park, North Carolina. Methane was supplied as pure gas (Air Liquide) and mixed with air *via* a system of mass flow controllers.

3. Results

Sensors prepared as described in the previous section consistently exhibited n-type behaviour, responding to the introduction of oxidizing gases with a resistance increase and to the introduction of reducing gases with a resistance decrease. They responded sensitively to the presence of NOx in dry air over a wide temperature range (Fig. 1). Interestingly the responses were complete within 5 minutes at low temperatures, but not at higher temperatures. The reverse was true for recovery, which was completed much more quickly at high temperatures than at low.

The base line resistances in dry air, taken from the data shown in Fig. 1 are plotted in Arrhenius form in Fig. 2. The activation energy for conduction of the sensor material, calculated from these data, was rather small (0.1 eV). The sensitivity to changes in operating temperature is thus much less than is the case for tin oxide which has an activation energy for conduction of 1.1 eV when dried and 0.28 eV when not dried.[7]

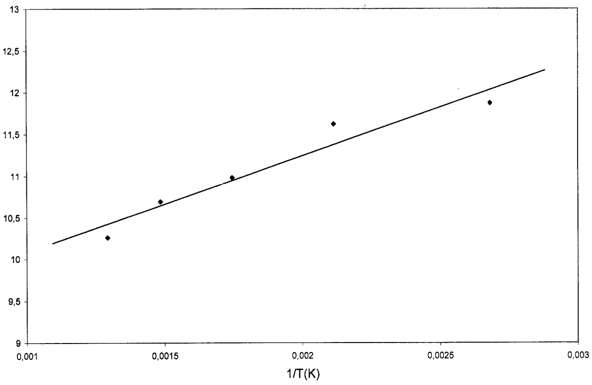

Fig. 2 An Arrhenius plot of the resistance in air data from Fig. 2 for a mixed molybdenum tungsten oxide sensor in the temperature range 100 to 500 °C. The slope yields an activation energy for conduction of 0.1 eV.

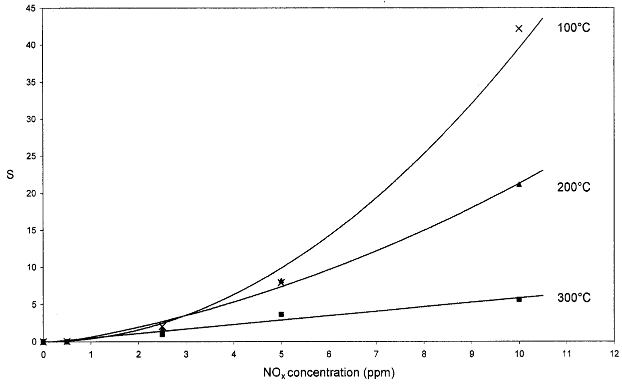

Fig. 3 Plots of the sensitivity, S $(=\Delta R/R_o)$, against concentration of NOx in air at temperatures of 100, 200 and 300 °C.

The variation of the sensitivity, S (expressed as change in resistance over resistance in air, $\Delta R/R_o$), with gas concentration shows an interesting dependence on temperature (Fig. 3). At 300 °C the sensitivity follows an almost linear dependence on concentration. At 200 °C the sensitivity increases markedly in the range between 5 and 10 ppm and at 100 °C the increase in sensitivity at high concentrations is at a higher level still. Decreasing the temperature from 300 to 100 °C results in a change in the sensitivity–concentration plot from approximately linear to approximately a concentration-squared dependence.

The potential interference from changes in relative humidity (RH) is rather small. For a maximum change in RH (from dry air to water-saturated air at room temperature), with the sensor operating at 300 °C, the change in conductance during the course of 5 minutes (Fig. 4) was very small, corresponding to a sensitivity of 0.33. The moisture responses at 200 °C and 400 °C

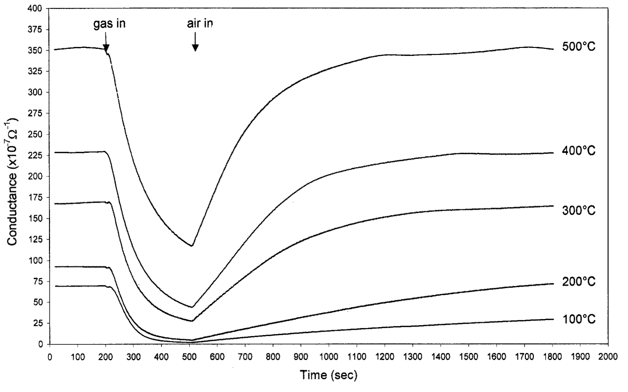

Fig. 1 A family of traces showing the responses of a mixed molybdenum tungsten oxide sensor to 10 ppm NOx in air at temperatures of 500, 400, 300, 200 and 100 °C.

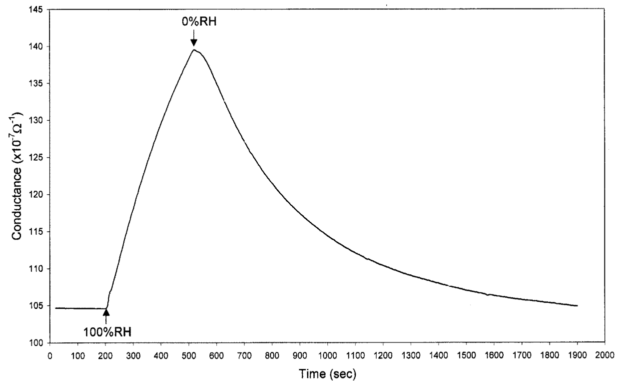

Fig. 4 Response of a mixed molybdenum tungsten oxide sensor operating at 300 °C to a change in atmosphere from dried air to air saturated at room temperature with water vapour.

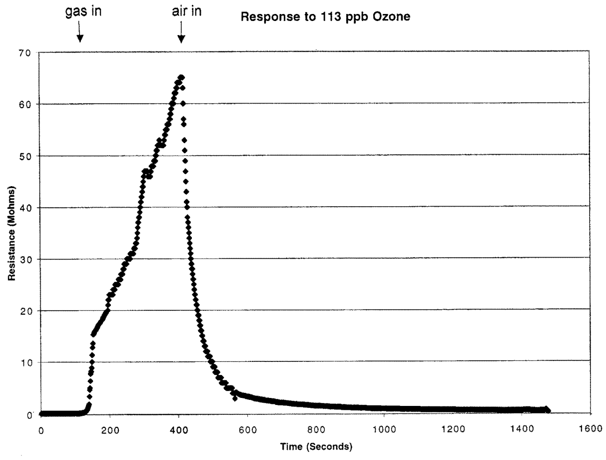

Fig. 5 Response of a mixed molybdenum tungsten oxide sensor operating at 300 °C to the introduction, at 100 seconds, of a pulse of ozone which ultimately reaches a concentration of 113 parts per billion. The rather irregular shape to the front end of the peak is due to instability in output flow from the ozone generator. The ozone flow was discontinued at 400 seconds.

were similar in magnitude to that shown in Fig. 4. Although the response shown in Fig. 4 is not complete within the 5 minute period, the response to a major change in relative humidity compares very favourably with the size of responses to gases within the same time interval, and also with the moisture response of tin oxide sensors. The equivalent change on a porous pellet of tin oxide at 300 °C yielded a sensitivity response of 10 000.[7]

The response to methane, a reducing gas, is very small. Exposure to 1% methane in air, even with the sensor operating at 600 °C only yielded a sensitivity response of 0.16.

Fig. 5 shows the response of the sensor at 300 °C when exposed to a growing pulse of ozone, which reaches a maximum of 113 parts per billion. The data are plotted in the form to show change in resistance in order to illustrate how large is the response. This response represents a sensitivity to 113 ppb ozone of almost 300.

4. Discussion

The results presented here indicate that the mixed molybdenum tungsten oxide is a potentially useful material for gas sensing, exhibiting a strong sensitivity to some gases present in low concentrations in air without any significant interference from changes in relative humidity. In view of the reports of favourable selectivity against interference from moisture in the case of sensors comprising WO_3[11] and MO_{3-x}, where M is predominantly molybdenum[10] it appears that oxides containing group 6 transition metal ions constitute a promising group of materials for gas sensor development.

Supplementary information will be needed in order to establish the mechanisms of response of the present sensors to oxidizing gases, particularly the subtle differences arising from the incorporation of molybdenum to tungsten trioxide. For instance, the sensitivity of sensors comprised of undoped tungsten trioxide reaches a maximum at an operating temperature of 200 °C[15] and is near zero at 100 °C. Thus the incorporation of a small amount of molybdenum reduces the temperature of maximum sensitivity and alters the forms of the sensitivity–concentration plots at the three temperatures where this was measured.

The unusual form of the low temperature response to NOx reported here (Fig. 3), and the relative speed of response at low and high temperatures respectively (Fig. 1) may provide some clue as to the mechanism of the response of these sensors. Two possible mechanisms might be conceived: the first based on competitive reaction kinetics, the second based on competitive chemisorption.

The interaction of the n-type semiconducting oxide with an oxidizing gas gives rise to an increase in resistance, most likely by decreasing the effective (near-surface) density of charge carriers (electrons). When charge carriers are removed from the oxide by surface reactions the equilibrium concentration of charge carriers is disturbed. The rate at which this equilibrium is restored and the rates of reactions taking place with oxidizing gas molecules will be influenced by temperature. One explanation of the results seen here would be that, at 100 °C, one of the reactions is quite fast and the other rather slow, giving the appearance of a steady state in a short period of time. At higher temperatures (*e.g.* 500 °C) the rate of the slow reaction has increased and the result of a competition between the two reactions is a relatively slow move towards true equilibrium. Such a situation would account for why the size of the response (the sensitivity) to 10 ppm NOx appears to be much larger at 100 °C than at 300 °C.

The second possible explanation is that, at low temperatures, NO_2 is in competition with weakly-bound oxygen species (*e.g.* O_2^-) for chemisorption sites, but at high temperature it is in competition with more strongly bound oxygen species (*e.g.* O^- or O^{2-}). Then at low temperatures the chemisorption of NO_2 is rapid, but the desorption and replacement by the weakly bound oxygen is slow. At high temperatures it is the displacement of the strongly bound oxygen which is the slow process and its readsorption which is fast. The size of the response could be understood if the NO_2 molecule replaced the oxygen species with the least electronic charge per oxygen atom (*e.g.* O_2^-) at the lower temperature and species with a higher electronic charge per oxygen (*e.g.* O^- or O^{2-}) at higher temperatures.

The size of the response to ozone is quite sufficient to allow monitoring of this gas around the National Ambient Air Quality Standard of 120 parts per billion.

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