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MoO_3-based sensor for NO, NO_2 and CH_4 detection

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Abstract

A sintered sensor element based on molybdenum oxide (MoO_3) has been fabricated. This sensor showed a good sensitivity towards NO and NO_2 gases in the temperature range of 200–500 °C. The resistance of the sensor element increased upon the introduction of NO and NO_2 gases. The sensor was also found to be suitable for methane gas; however, it showed a decrease in the resistance upon introduction of the gas. Satisfactory performance of the present sensor to NO_2, NO and CH_4 at concentrations of 100, 250 and 500 ppm, respectively, was obtained.

Keywords: Molybdenum oxide; Gas sensor; Lattice oxygen; Electrical resistivity

1. Introduction

The application of sensors has been increasing on an astonishing pace in the past few years as the operation of our industrialized world heavily depends on sensors for various purposes such as security devices, increased automation, and most importantly, for gas sensing and for environmental and emission monitoring. A variety of materials have been used for gas sensing, which include electronic ceramics, oxide semiconductors, solid electrolytes, and conducting polymers [1–5]. Gas sensors give an electrical output, measuring the change in property such as resistance or capacitance.

Nitrogen oxides, NO and NO_2, produced from combustion facilities and automobiles are the chief pollutants which damage human respiratory organs and nerves. They also cause acid rains. Production of methane gas is also a major source of green house effect. However, there are few reliable and precise sensors for these toxic gases. Akiyama et al. [6] demonstrated the use of WO_3-based gas sensor to be an effective means for the detection of NO and NO_2 gases. This work led to a spate of investigations by others who fabricated WO_3 films (thin, thick and nanocrystalline) using different techniques such as sputtering, spray pyrolysis and chemical methods [7–10] to improve upon the sensor sensitivity, selectivity and response characteristics.

Molybdenum oxide (MoO_3) which has similar physical and chemical characteristics to WO_3 has recently drawn a lot of attention with regard to its gas-sensing ability [11–18]. In the present work, we explore the gas-sensing capability of sintered MoO_3. The basic design of this sensor is akin to that used by Akiyama et al. [6]. Preliminary results are encouraging and suggest that MoO_3 could serve as a possible sensing material not only for NO_x gases but also for methane gas.

2. Experimental

High purity MoO_3 (particle size ranging between 0.5 and 2 μm) was procured from BDH, India. MoO_3 paste was prepared using deionized water and a few drops of a binder. The paste was applied to an alumina substrate which has been provided with two stainless steel electrodes separated by a distance of about 3 mm, and sintered at 550 °C for about 6 h in air. The sintered element is shown in Fig. 1. The gas-sensing experiments were performed using a standard flow apparatus with a built-in heating facility through which the test gas was allowed to flow at a rate of 150 cm^3/min. The test gas was prepared by diluting NO and NO_2 gases with dry air. The concentration of NO and NO_2 were fixed at 250 and 100 ppm, respectively. The sensing capability of the sensor was registered by monitoring the change in the electrical resistance of the sensor element upon switching-on and -off of the sample gaseous species. The experiments were carried out in the temperature range of 200–500 °C. The sensitivity of the

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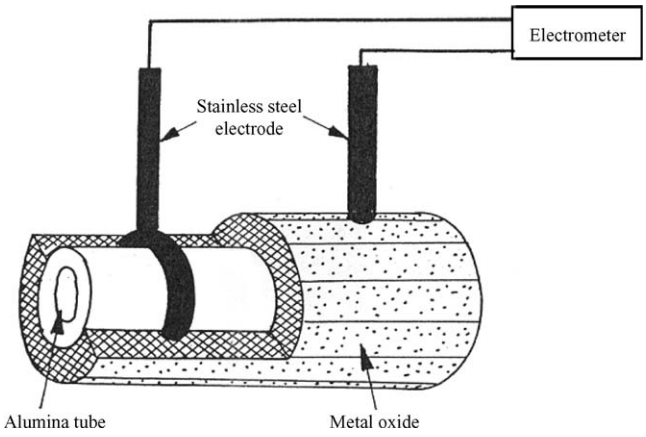

Fig. 1. Schematic representation of the set-up for sensor element.

sensor is defined as R_{gas}/R_{air} for oxidizing gases (NO and NO_2), and R_{air}/R_{gas} for the reducing gas (methane), where R_{gas} and R_{air} are the electrical resistances of the sensor in the measuring gas and in clean air, respectively.

3. Results and discussion

MoO_3 is an n-type semiconductor with an oxygen deficiency. Its bandgap is 3.2 eV [19] and its electrical resistivity at room temperature is of the order of $10^{10}\,\Omega$ cm [20]. The response transients of MoO_3-based sensor to the exposure of 250 ppm NO and 100 ppm NO_2 as a function of temperature are displayed in Figs. 2 and 3A, respectively. When the test gases are switched on, the resistance of the sensor element increased and attained a saturation value rapidly. The resistance almost (90%) recovered its original value when the gases were turned off. This decrease in the resistance on switching off the gases is faster than the rise that took place on the introduction of gases. The response times ranged between 20 and 40 s at 400 °C. The response times at temperatures lower than 200 °C were not reliable due to the high resistance offered by the sensing element. It can be seen that sufficiently high sensitivity could be achieved using MoO_3 material.

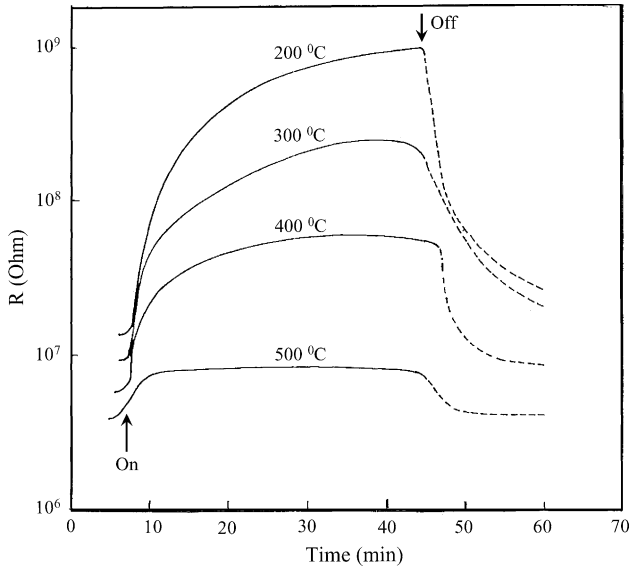

Fig. 2. Response characteristics of a MoO_3-based sensor to 250 ppm NO gas.

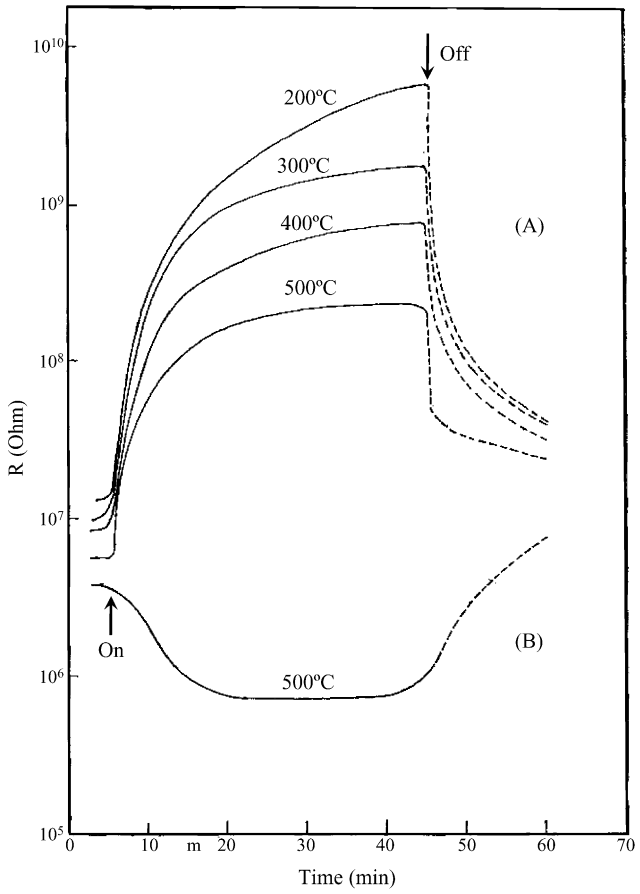

Fig. 3. Response characteristics of a MoO_3-based sensor to: (A) 100 ppm NO_2 and (B) 500 ppm CH_4 gases.

The present sensor was also found to be suitable for the detection of methane (CH_4) gas. The transient response of MoO_3-based sensor to the exposure of 500 ppm CH_4 at 500 °C is shown in Fig. 3B. In this case, however, the resistance of the sensor decreased upon introduction of the gas and the transient response was almost a mirror image of those obtained for NO_x gases.

The electrical conductance of semiconducting oxide-based gas sensor depends on the chemisorbed oxygen ions, oxygen vacancies and the interstial ions. The gases to be sensed cause a change in the oxygen balance of the oxide sensor, leading to a variation in its conductance. It is believed that in most of the semiconducting oxide-based sensors, the chemisorbed oxygen is involved in their sensing action [21–23]. It has, however, been shown that the sensing mechanism in MoO_3 did not involve chemisorbed oxygen but rather the lattice oxygen of MoO_3 [14,24,25], as shown below for the case of a reducing gas, R, in terms of Kroger–Vink notation:

$$O_O \rightarrow V_O^{2+} + O_i^{2-} \quad (1)$$

$$R + O_i^{2-} \rightarrow RO + 2e^- \quad (2)$$

where O_O is the lattice oxygen, V_O^{2+} the oxygen vacancy in the lattice, and O_i^{2-} is the interstitial oxygen. It can be seen from