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A self-heating gas sensor with integrated NiO thin-film for formaldehyde detection

Chia-Yen Lee [a], Che-Ming Chiang [b], Yu-Hsiang Wang [a], Rong-Hua Ma [c,*]

[a] Department of Mechanical and Automation Engineering, Da-Yeh University, Changhua 515, Taiwan
[b] Department of Architecture, National Cheng-Kung University, Tainan 701, Taiwan
[c] Department of Mechanical Engineering, R.O.C. Military Academy, No. 1, Weiwu Rd., Fengshan, Kaohsiung 830, Taiwan

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Abstract

This study develops a MEMS-based formaldehyde gas sensor based on a suspended silicon nitride microstructure with an integrated micro Pt heater, a thin-film NiO sensing layer and Pt interdigitated electrodes (IDEs) to measure the resistance changes of the NiO layer in the presence of formaldehyde. A specific orientation of the NiO layer is observed as the substrate temperature in the sputtering process is increased. The increase in substrate temperature assists in the formation of a NiO layer with the correct stoichiometric ratio (1:1). When formaldehyde is present in the atmosphere, oxidation occurs near the heated NiO sensing layer. This oxidization causes a change in the electrical conductivity of the NiO film, and hence changes the measured resistance between the interdigitated electrodes. The formaldehyde concentration is then determined from the change in the measured resistance. The application of a voltage to the Pt heaters causes the temperature of the micro-hotplate to increase, which in turn enhances the sensitivity of the sensor. The current experimental results show that the sub-micrometer grain sizes of the sputtered oxide thin film yield a high degree of sensitivity ($0.33\,\Omega\,\mathrm{ppm}^{-1}$), a low hysteresis value (0.7 ppm), a detection capability of less than 0.8 ppm, a quick response time (13.2 s), a quick recovery time (40.0 s) and a high selectivity over a wide range of formaldehyde concentrations in the presence of interfering species, such as acetone, ethanol and methanol. The novel micro formaldehyde gas sensor developed in this study is ideal for applications aimed at preventing and controlling sick building syndrome (SBS).

Keywords: Formaldehyde; Gas sensor; Micro-hotplate; MEMS; NiO thin film; Sick building syndrome (SBS)

1. Introduction

Sick building syndrome (SBS) is a significant health issue nowadays. SBS describes the medical phenomenon in which occupants of a building experience acute health effects, which appear to be related to the time spent in a building, but cannot be traced to any specific illness or cause. SBS has been defined as a set of diffuse and irritative symptoms predominantly involving the eyes and the respiratory organs [1]. While the specific origins of SBS remain unclear, it is thought that the contributing factors to SBS include chemical contaminants from outdoor and indoor sources, biological contaminants and inadequate ventilation. The indoor air pollution caused by chemical contaminants contained in construction materials has attracted particular attention since these compounds appear to be strongly associated with the occurrence of SBS. Indoor air pollution is caused primarily by sources within the building. For example, adhesives, upholstery, carpeting, copy machines, wood products, cleaning agents and pesticides may all emit volatile organic compounds (VOCs), including formaldehyde (HCHO) [2]. Formaldehyde is a widely used commercial chemical due to its chemical activity, high purity and relative cheapness. However, various risk factors have been identified with this particular chemical [3,4]. It has been shown that throat and nasal irritation can occur at formaldehyde levels as low as 0.08 ppm [5]. Accordingly, the National Institute for Occupational Safety and Health, USA (NIOSH) has established a permissible long-term exposure limit of 1 ppm [6].

Historically, the detection of formaldehyde has generally been achieved using a stringent semi-batch air-sampling procedure, followed by a batch analysis of the sample gas chromatography/mass spectrometry (GC/MS). Clearly, this procedure is

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* Corresponding author. Tel.: +886 7 7466641; fax: +886 7 3474453.
E-mail address: rh.ma@msa.hinet.net (R.-H. Ma).

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unable to provide formaldehyde exposure information on a real-time basis. Hence, a number of researchers have developed optical sensors for formaldehyde quantification applications [7–10]. However, the associated optical arrangements tend to be rather bulky and elaborate. Over the past decade, emerging MEMS technologies and micromachining techniques have contributed significantly to the miniaturization of sensors. As a result of advances in MEMS technology, sensing instrumentation is now available capable of accessing information at a micro-scale level [11–13]. Importantly, the sensitivity and performance of these micro sensors can be enhanced through their integration with submicron/nano-scale materials and with other micro devices. Recently, Dirksen et al. [6] fabricated NiO thin-film formaldehyde gas sensors by dipping alumina substrates in a nickel acetylacetonate solution to form thin NiO films of thickness 0.5 μm. It was found that the conductivity of these films changed as the formaldehyde concentration was varied at temperatures ranging from 400 to 600 °C. At approximately 3 μm, the sintered grain size was rather large and was hence expected to reduce the sensitivity of the device. However, a linear formaldehyde sensitivity of 0.825 mV ppm^{-1} was attained at a temperature of 600 °C. Although, the sensor demonstrated a high sensitivity, its detection limit was only 50 ppm, i.e., far higher than the prescribed "maximum permissible long-term exposure" limit of 1 ppm. Furthermore, the proposed sensor lacked an integrated heating device capable of maintaining the optimal working temperature of 600 °C. Therefore, the sensor operation required the use of an external heater, which not only increased the bulk of the sensor arrangement, but also increased its power consumption. As a means of overcoming this problem, Lee et al. [14] proposed the use of Pt resistors as integrated micro-heaters for MEMS-based temperature control systems. Pt was chosen specifically as the resistor material on account of its physical and chemical stability.

The present study develops a novel simplified process for fabrication of a MEMS-based formaldehyde sensing device featuring micro-hotplates with integrated Pt resistance heaters, a sputtered NiO layer with sub-micrometer grain sizes and Pt interdigitated electrodes (IDEs). The experimental results indicate that the proposed sensor has a high degree of sensitivity (0.33 Ω ppm^{-1}), a low hysteresis value (0.7 ppm), a detection capability of less than 0.8 ppm, a rapid response time (13.2 s), a quick recovery time (40.0 s), a high selectivity over a wide formaldehyde concentration range in the presence of interfering species, such as acetone, ethanol and methanol and a simple configuration with no requirement for any form of external heating device.

2. Sensor design

2.1. Catalysis

A catalyst is an agent, which accelerates reactions, which are thermodynamically favored but kinetically slow. Metal clusters and oxides are both suitable catalysts for oxidation reactions. In the current investigation involving the oxidation of formaldehyde, two particular oxidation reactions are of interest, namely:

$$\text{HCHO}_{(g)} + \tfrac{1}{2}\text{O}_{2(g)} \rightarrow \text{HCOOH}_{(g)}$$

and

$$\text{HCHO}_{(g)} + \text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(g)} + \text{CO}_{2(g)}$$

The former reaction produces formic acid, while the second produces water and CO_2. Dirksen et al. [6] listed all of the catalysts used for the oxidation of formaldehyde, and reported that the most active catalytic oxide appeared to be NiO. The electrical conductivity of these oxides is significantly dependent on the oxygen partial pressure in the atmosphere. This phenomenon can be exploited to sense the concentration of a gas causing a catalytic oxidation on the surface of the oxide. The resulting reactions decrease the partial pressure of the oxygen at the oxide surface and hence alter the electrical conductivity of the oxide. The change in electrical conductivity is then detected in the form of an electrical signal whose magnitude is dependent upon the rate of catalytic oxidation of the gas [15].

When formaldehyde is present in the atmosphere, it is adsorbed into, and subsequently reacts with, the sensing layer provided that the applicable thermodynamic conditions are favored. As a result of this reaction, the surface coverage of atomic oxygen decreases. Since the electrical conductivity of the sensing layer is proportional to the nickel cation concentration of NiO [16], its conductivity increases through the adsorption and reaction of formaldehyde. This conductivity increase leads to a reduction in the measured resistance. Furthermore, the increased partial pressure of formic acid in the atmosphere generated by the formaldehyde oxidation reaction further decreases the surface coverage of the atomic oxygen, hence increasing the electrical conductivity [6].

2.2. Micro-hotplate

The gas sensor developed in this study operates on the principle that changes in the coverage of the adsorbed or chemisorbed gas species on the sensing film cause a detectable change in the electrical properties of the film, and particularly in its conductance. Gas sensing devices are typically designed to operate at elevated temperatures in order to activate the reactions, which produce a sensor response and to reduce humidity effects [17]. However, a drawback of these devices is that the observed response may actually be the result of the presence of more than one gases. To enhance the "selectivity" of a device, its operating temperature must be optimized in order to reduce the effects of competing reactions. In the present study, Pt micro heaters are fabricated on a suspended plate to heat the formaldehyde sensing layer of the developed gas sensor. When a voltage is applied to these heaters, the temperature of the micro-hotplate increases and subsequently attains a constant temperature at a constant applied voltage. Applying a voltage to the heaters generates a simultaneous heating effect in the thin-film sensing element since it is deposited directly on the hotplate. The optimal operating temperature can be determined by varying the temperature of the hotplate and comparing the