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Design, fabrication, and testing of MEMS-based miniaturized potentiometric nitric oxide sensors

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ABSTRACT

We report on the development of miniaturized potentiometric nitric oxide (NO) sensors. This work covers the design, fabrication and testing of these NO sensors. In particular, microelectromechanical systems (MEMS) fabrication techniques were utilized to miniaturize the size of the sensors. Sensors were fabricated using both shadow mask and photoresist mask fabrication methods. Arrays of up to 15 sensors were electrically connected in series during the fabrication process to improve the signal of the overall device for a given NO concentration. Testing on these sensor arrays toward NO was carried out at 550 °C to compare the performance of the various designs of the sensor. Sensitivity below the ppm level was demonstrated with the photoresist-masked 15-sensor array. Long-term stability of the miniaturized sensor array when operating at high temperatures needs to be improved before practical applications of this MEMS sensor technology can be realized.

1. Introduction

The need for nitric oxide (NO) sensing is critical in a diverse variety of applications ranging from high temperature combustion [1–5] to clinical analysis [6,7]. An example of a high temperature combustion application is monitoring and minimization of NO_x emissions produced by lean burn engines [8]. For these and other combustion-based applications, NO sensors that are high temperature capable are critical. A very different area where NO sensing is also required is in the medical industry, specifically in breath analysis for diagnosis of respiratory ailments. In this application much lower (ppb) NO concentrations must be detected [9–11]. This interest in the combustion and medical community has spurred the development of NO sensing devices. Several technologies are being developed [12–16]. A variety of solid-state electrochemical sensors for NO has been demonstrated previously [17–20], and strategies to improve their performance have been investigated [17,21,22]. Solid-state potentiometric electrochemical sensors have the potential to detect NO over a wide range of concentrations. Such sensors combine versatility, sensitivity, and ease of use with relatively low cost and have the added benefit of being easier to miniaturize compared to other technologies.

We have recently demonstrated the series connection of potentiometric NO sensors to increase sensitivity [7]. A series of 10 and 20 sensor arrays were found to detect NO at ppb concentrations. However, the sensor arrays reported had dimensions of 5–10 cm in length as the sensors were made individually by hand and assembled into arrays by hand. This manual fabrication limits the minimum size to which the sensors can be reduced, while also limiting mass reproducibility and the ability to decrease their cost. Miniaturized sensors based on MEMS (microelectromechanical systems) fabrication technology have been demonstrated for aerospace applications [23–25]. A reduction in size of the sensors using MEMS techniques would not only provide better implementation in a variety of size constrained applications, but the reduced size would also decrease the power required to heat the sensors to operating temperature (from watts to hundreds of milliwatts). In addition, the application of MEMS fabrication techniques allows for multiple sensors to be made at one time, thereby reducing costs. A previous report in the literature on miniaturization of series connected potentiometric sensors was focused on oxygen sensors [26]. In this paper, we report on the first MEMS-based fabrication of miniaturized arrays of high-temperature, series-connected potentiometric NO sensors, and include here details on the fabrication process.

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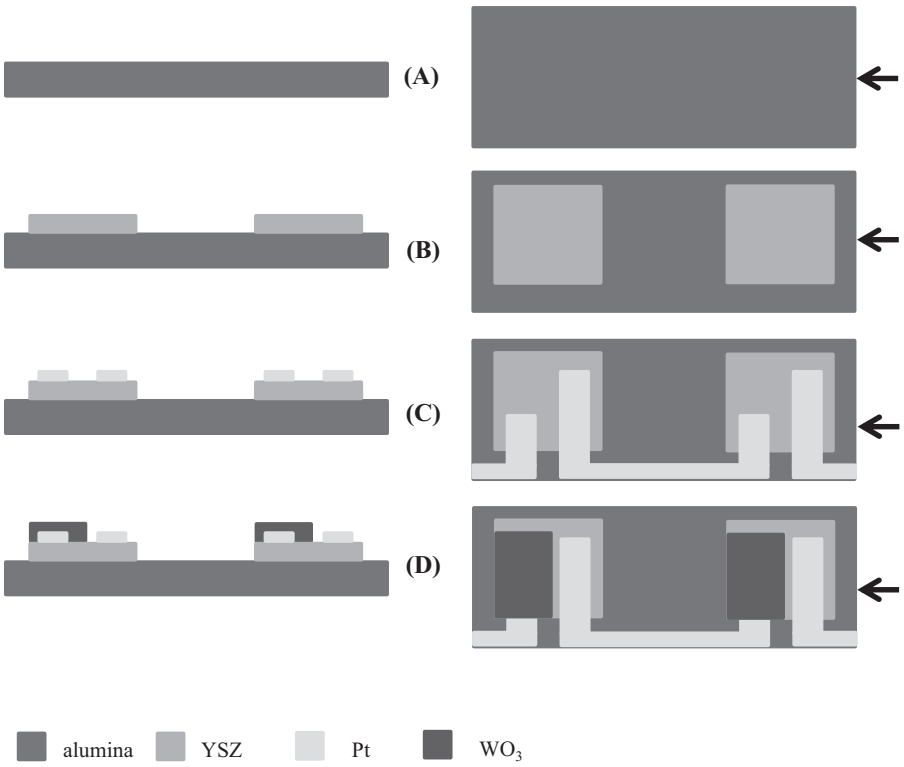

Fig. 1. Fabrication process flow for microfabricated NO sensors. Cross sectional and top views are shown left and right, respectively. (a) Alumina substrate, (b) deposition of YSZ islands, (c) deposition of Pt electrodes, (d) sensor after deposition of WO_3. Arrows indicate where cross section is taken through.

2. Experimental

The NO sensor reported in this work is an electrochemical sensor whose structure consists of solid electrolyte and reference and working electrodes. An electric potential difference (ΔV) is induced between the working and reference electrodes when NO impinges on the sensor due to the dissimilar chemical activity at each electrode. The reference electrode is platinum (Pt), while the sensing or working electrode is tungsten oxide (WO_3). The solid electrolyte is yttria-stabilized zirconia (YSZ). These sensor material choices are based on larger hand-made sensors that were demonstrated previously [7].

The NO sensors were fabricated on aluminum oxide substrates. Each sensor on the substrate was built on a YSZ island on the substrate. Pt reference and WO_3 working electrodes were located on opposite sides of the YSZ island. A Pt pad was located below the WO_3 to make contact to this working electrode. As each sensor was an individual electrochemical cell, multiple sensors could be connected in series to generate a larger signal response and improve the signal response to NO. The sensors were electrically connected together as in the cells of a battery such that the induced ΔV's were additive, thereby increasing the response for a given NO concentration over a single sensor. Sensor arrays of 5, 10, and 15 sensors were connected electrically and tested. Each sensor array was interconnected electrically via Pt thin-film leads.

2.1. Fabrication

The sensors were batch fabricated using a MEMS fabrication approach, with each two-inch alumina wafer containing multiple devices. These MEMS-based NO sensors were fabricated using masks and thin film deposition techniques. Two alternative methods of masking were used in the sensor fabrication, one using thin metal shadow masks and another using photoresist masks, as described below. The sensor arrays consisted of one to three rows of five sensors.

The general process flow for the sensors is shown in Fig. 1. The YSZ islands were sputter deposited using the first mask, forming individual rectangular islands of YSZ. A thermal anneal was then carried out to densify the YSZ. The Pt electrodes and electrical interconnects were then deposited using the next two masks. Finally, the WO_3 was deposited from a tungsten target in an argon/oxygen ambient using the third mask. The sensors were then diced into individual arrays following the final film deposition.

The three films that were deposited were the YSZ, Pt, and WO_3 films. Both the YSZ and Pt films were deposited by sputtering YSZ and Pt targets, respectively. The WO_3 was deposited by a reactive sputter deposition process whereby a tungsten (W) target was sputtered in Ar/O_2 to produce WO_3. The deposition was carried out at 15 mTorr using 200 W DC power, at a rate of 0.333 Å/s. XPS analysis on the films confirmed the proper stoichiometry of the WO_3 films after the sputter deposition processes, as shown in Fig. 2.

The sensors were fabricated using one of two methods to define each deposited film. The first method utilized was based on shadow masks, where a metal mask was used during each of the deposition processes to define the deposited films into the desired features. The metal masks were placed onto the substrate and clamped at the edges of the substrate. The shadow masks were aligned manually from one mask layer to the next using alignment marks, prior to clamping. The second fabrication method utilized for the sensors was based on the use of photoresist masks, and a lift-off process for definition of the deposited films on the substrate. In the photoresist process, a photoresist film was spin coated onto the surface of the substrate and then baked. A mask was placed in contact with the photoresist and the assembly was then exposed to UV light and developed to define openings in this layer for deposition of a film. Once the sputter deposition process was finished, the sputtered film was defined by a lift-off process whereby the photoresist was