A Methanol Sensor Incorporating Nanostructured ZnO and Integrated Micro-heater on Thermally Isolated Planar MEMS Platform

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***Abstract*—A sensor incorporating nanostructured zinc oxide film on planar and thermally isolated MEMS platform is reported for detecting methanol vapours. An innovative technique for fabricating sensor having integrated microheater with improved mechanical strength is presented. The proposed innovation facilitates the sensor to achieve desired temperature on the chip at lower power. The sensors are capable of detecting methanol vapours at 50 °C and at room temperature (30 °C) with slightly reduced sensitivity. To achieve the operating temperature of 50 °C and 30 °C, the sensor requires only 40 and 20 mW of power respectively. The lower operating temperature has been achieved due to the use of nanostructured material as sensing layer. The sensor is capable of giving detectable response for concentrations of methanol vapor as low as 5 ppm.**

Keywords- Nanostructured ZnO; Thermal evaporation; MEMS Platforms; Methanol sensor.

I. INTRODUCTION

In many industries, gases and volatile organic compounds (VOCs) are increasingly being used as raw materials and for this reason, it has become very important to develop highly sensitive detectors for these compounds. It is desirable that such devices should continuously monitor the VOCs and gases in the environment in quantitative and selective manner [1]. However, many of these devices have not yet reached commercial viability because of problems associated with the production worthiness of the gas sensing technologies. Selectivity, power consumption on account of heating requirements of the sensing layer and reliability are some of the issues which have not been adequately resolved for these sensors to be deployed on a large scale [2]. With the increasing demand for better gas sensors of higher sensitivity and greater selectivity, intense efforts are being made to find more suitable materials with the required surface and bulk properties for use in gas sensors. Detection and quantification of gaseous species in air as contaminants (polluting gases) at low cost is also becoming important.

The metal oxides have been explored and used as sensing layers in gas / VOC sensors for more than a decade [3, 4-10]. ZnO is one of the prominent metal oxide materials, which has been extensively investigated for gas/VOC sensors. This arises because of the high mobility of conduction electrons and good chemical and thermal stability under the operating conditions. The use of nano-structured materials for the sensing device is envisaged to further improve the sensitivity of these devices at lower operating temperature [1-2, 11]. This is attributed to enormously increased surface to volume ratio compared to their thin films.

The sensors based on metal oxide materials operate at elevated temperatures (~ 300 °C) which results in higher power consumption [4, 8, 10]. To reduce the heat loss and thus power consumption, the thickness of the substrates is selectively reduced [12]. The thinning of the substrate results in reduced mechanical strength of the substrate. As a result, extra care is required during packaging. The yield also becomes an important issue.

In the present work, the sensors are fabricated using two different techniques: (a) on suspended diaphragm of SiO_2 (~2 μm) and (b) thermally isolated planar platform. The proposed innovation facilitates the sensor to achieve desired temperature on the chip at lower power. The sensing film in both the cases is nanostructured ZnO. The sensors are capable of detecting the methanol vapours in the range of 5-50 ppm at fairly low operating temperature of 50 °C. Furthermore, the power consumption is also considerably reduced without compromising the mechanical strength of the substrate in the planar type thermally isolated platform presented here. To the best of our knowledge, this type of performance is not reported in the published literature.

II. EXPERIMENTAL WORK

A schematic drawing of the sensor on suspended diaphragm is shown in Fig. 1 and the corresponding process flowchart is shown in Fig. 2. The sensor was fabricated using 7-masks process sequence and used a combination of bulk-surface micromachining technique [13]. The starting silicon wafers were 280 μm thick, n-type, having 5–10 Ω-cm resistivity and (100) orientation. A layer of SiO_2 (1 μm) was grown by thermal oxidation process. A window was opened on front side of the wafer by lithography technique (mask #1) and a pit (2.5 mm x 2.5 mm and 5 μm depth) was formed using bulk micromachining which was carried out in 40% KOH solution at a temperature of 80 °C. ZnO was then deposited as sacrificial layer using RF magnetron sputtering technique and its thickness was chosen to be somewhat more than the pit depth [13, 14].

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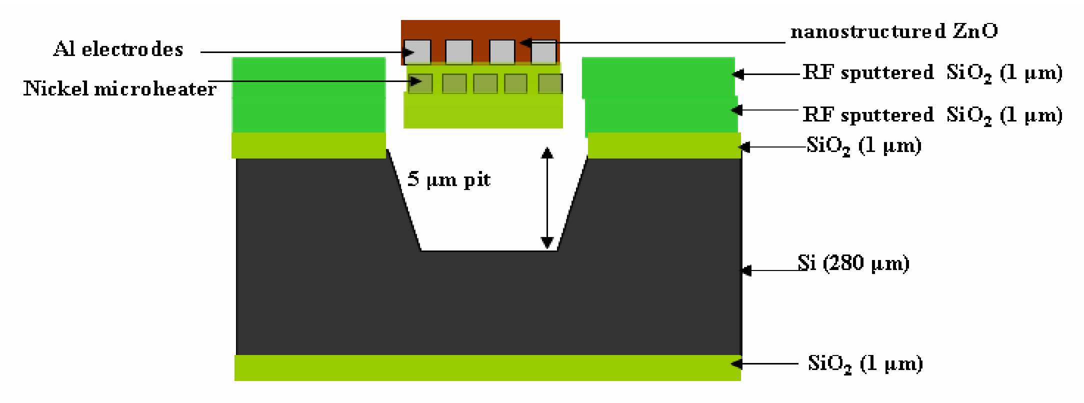
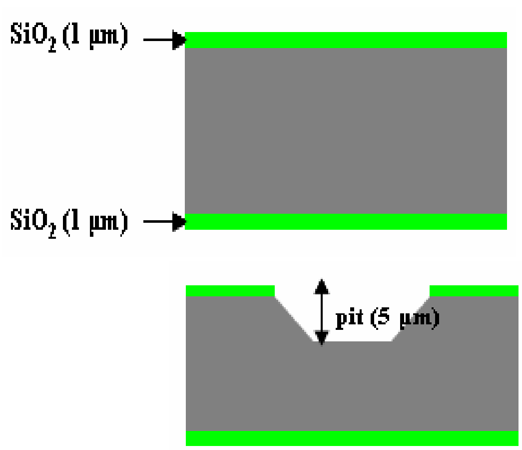
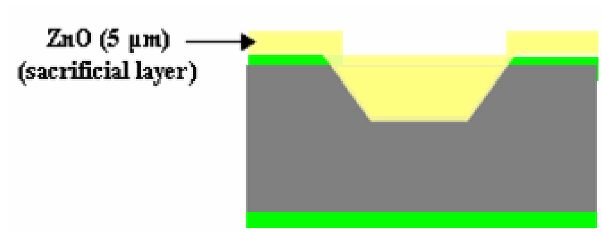
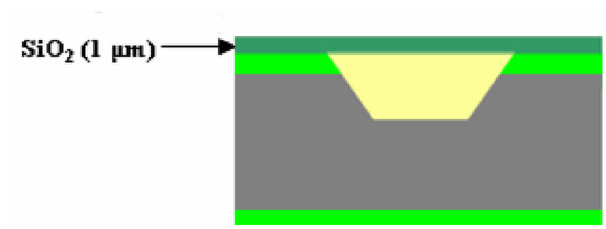


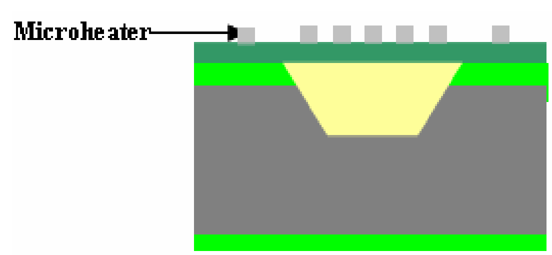
Figure 1. A schematic diagram of the MEMS gas sensor on a suspended platform.

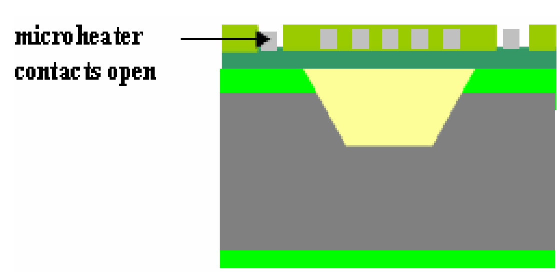
The pit was planarized using lithography process (mask #2) followed by chemical mechanical planarization (CMP). Silicon dioxide layer (1 µm) was then sputter deposited on the wafer in the next step. A layer of nickel (0.3 µm thickness) was then deposited using RF diode sputtering over this SiO_2 layer. The Ni layer was then patterned using photolithography to form the microheater (mask #3). Over this, a layer of SiO_2 (1 µm) was again sputter deposited. The purpose of this layer was to electrically isolate the heater and the aluminum inter-digital electrodes to be formed in the next step. The SiO_2 from the microheater contacts was removed (mask #4). The aluminum layer of 0.8 µm was then deposited by thermal evaporation and patterned to form the sensing inter-digital electrodes (mask #5). A Zn film (0.3 µm) was selectively deposited using lift-off technique (mask #6) and annealed at 300 °C for 12 h in air ambient. The lift-off technique was used for patterning Zn as the etchant for Zn [HCl-DI water solution (1:100 by volume)] affects the Al. As the last step, the sacrificial layer was etched to complete the fabrication. The sacrificial layer etching was accomplished through lateral etching initiated from four windows formed outside the sensor area using photolithography (mask #7), as illustrated in the Fig. 2 and Fig. 5.











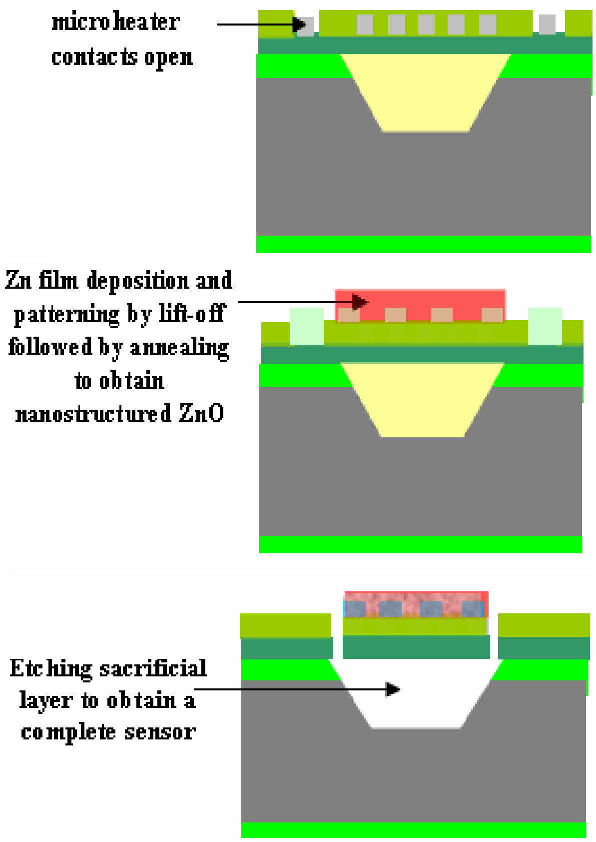


Figure 2. Process flowchart of sensor fabricated on suspended diaphragm.

In the second approach, the sensor was fabricated on a thermally isolated planar platform without using a suspended diaphragm. The blown-up diagram of the sensor fabricated using this technique is shown in Fig. 3 and the corresponding process flow is shown in Fig. 4.

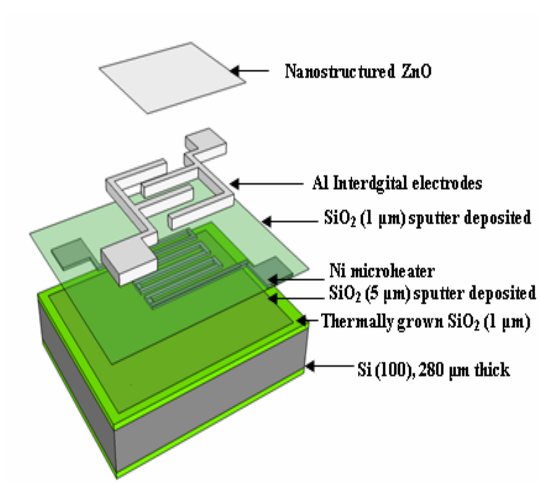


Figure 3. Blown-up diagram of the sensor fabricated on thermally isolated planar platform.

The sensor fabrication requires a 6-mask process sequence. The starting silicon wafers used were 280 µm thick, n-type, having 5–10 Ω-cm resistivity and (1 0 0) orientation. A layer of SiO_2 (1 µm) was grown by thermal oxidation process.

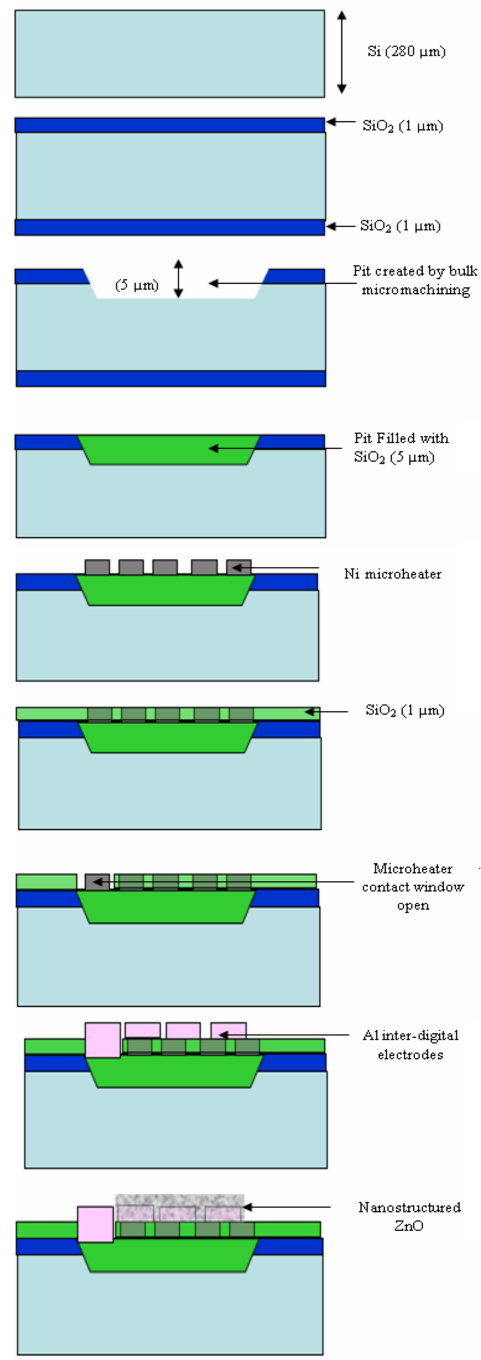
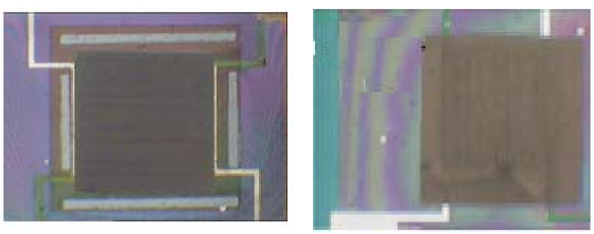


Figure 4. Process flow for sensor fabrication on thermally isolated planar platform and corresponding optical photographs at different steps.

A window was opened on front side by lithography technique (mask #1) and a pit (5mm x 5mm and 5 µm depth) was formed using bulk micromachining which was carried out in 40% KOH solution at a temperature of 80 °C. The pit was filled by SiO_2 deposited by RF magnetron sputtering process. The pit was planarized using photolithography (mask #2) and CMP. The rest of the process steps are identical to those used in the previous design. The advantage of fabricating sensor using the above mentioned process is that the complete sensor is fabricated on silicon substrate using trench formation, backfill and CMP. Thus there is no diaphragm or hanging structure. The mechanical strength of the substrate is retained in this approach. The optical photographs of the sensors fabricated on suspended diaphragm (2 µm) and on thermally isolated platform are shown in Fig. 5.



(a) **(b)**

Figure 5. Optical photograph of sensor fabricated on (a) diaphragm (2 µm) and (b) using thermally isolated platform technology.

III RESULTS AND DISCUSSION

Fig. 6 shows the plot of power consumption versus temperature for the sensors fabricated on suspended diaphragm (2 µm) and sensor fabricated using thermally isolated platform.

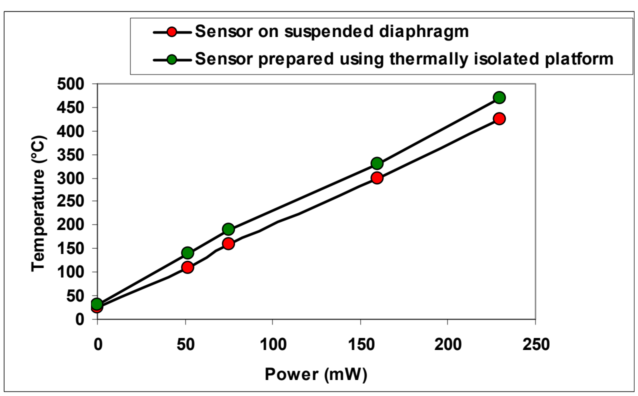


Figure 6. Power versus temperature plot of microheater fabricated on suspended diaphragm (2 µm) and sensor fabricated using thermally isolated platform technology.

It can be concluded that the electrical power required to raise the temperature of the sensing layer to required level is considerably reduced because of improved thermal isolation of the sensor fabricated on suspended diaphragm. For example, a temperature of 175 °C is reached at a power of 80 mW for a sensor prepared on suspended diaphragm and same temperature is achieved at a power of 90 mW for sensor fabricated using thermally isolated platform technology. In contrast, the power consumption for the same operating temperature of the sensor made on conventional silicon substrate has been simulated and measured to be about 235 mW. The advantage of using thermally isolated planar platform technology is that the mechanical strength of the substrate is not compromised while the power consumption is also very low.

The SEM image of nanostructured ZnO film is shown in Fig.7. The VOC sensing results of the sensors fabricated on thermally isolated platform are now presented. The sensor was tested for methanol vapors in a closed chamber [15]. The sensor was heated to different temperatures by applying power to the integrated heater. The methanol vapors were introduced in the chamber by bubbling N_2 through the methanol maintained at room temperature (20 °C). The desired concentration of the vapors was obtained in the chamber by controlling the flow rate of N_2 through methanol and adding pure air through a separate gas line [15].

The flow rates were measured and controlled using precision flow meters. The concentration of methanol vapors was calculated using the following equation [16].

$$C = \frac{\dfrac{P^* \times L}{760 - L}}{\dfrac{P^* \times L}{760 - L} + L + L^*} \times 10^6 \tag{1}$$

where, L and L* are gas flow rates of N_2 (through the bubbler) and air respectively. P* is the vapor pressure of the methanol (in mm of Hg) at room temperature (20 ºC).

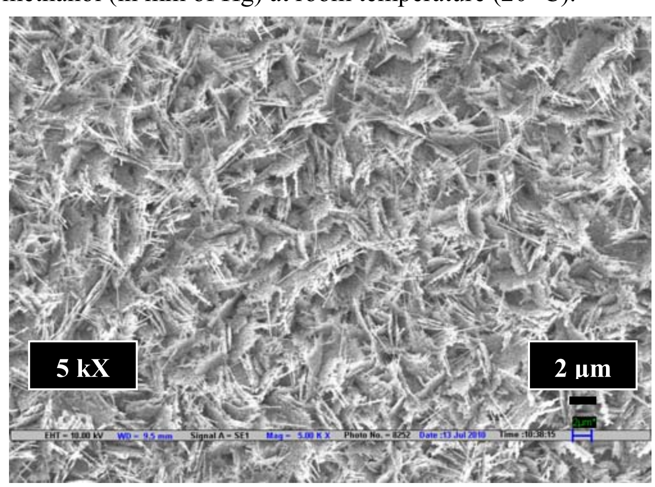


Figure 7. SEM image of ZnO nanocombs obtained after annealing Zn film (300 nm) at 300 °C for 12 h.

The focus of the present work is to develop energy efficient sensors that can operate near room temperature. This is an important consideration for the sensors to be deployed at remote places and are battery operated. The power consumption becomes an important issue. Accordingly, one of the primary aims of the present work is to develop the sensor, which can give appreciable response at lower operating temperatures. This will result in lower power consumption of integrated microheater thereby prolonging the life of the battery. It was observed that at 50 °C, the power consumption of the microheater was significantly less as compared to the corresponding value at 150 °C. Also, the sensor response at 50 °C is appreciable. A comparison of the sensor response at 30, 50, 100 and 150 °C is presented in Fig. 8 to illustrate this point.

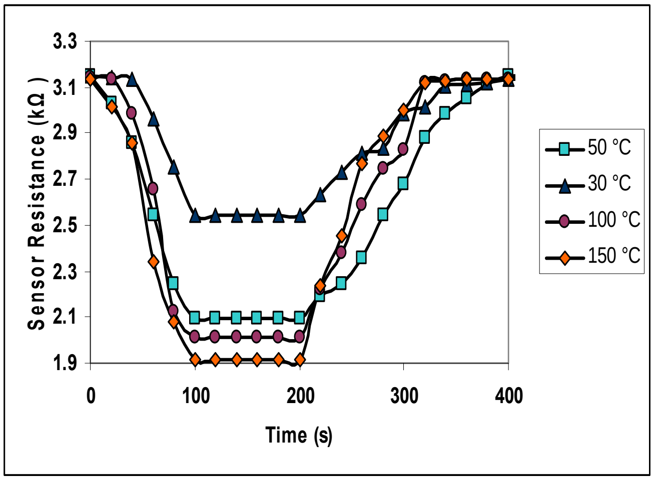


Figure 8. Response of the sensor to 50 ppm of methanol vapors at different operating temperatures.

The response of the sensor at 50 °C for other VOCs is shown in Fig. 9. It can be clearly observed that the sensor shows detectable change in resistance at such a low operating temperature. It was observed that at 50 °C, the change in sensor resistance is significant for methanol vapors as compared to other VOCs. This shows that at operating temperature of 50 °C, the sensor is somewhat selective to methanol. The power required to achieve temperature of 50 °C is only about 40 mW.

The dynamic response of the sensor to different concentrations of methanol vapors at 50 °C operating temperature is shown in Fig. 10. The sensor is capable of detecting methanol vapors down to 5 ppm level. The sensor showed repeatable response with response time of 80 s and recovery time of about 120 s. The large values of response and recovery times are attributed to the large size of the chamber used for testing and does not represent the inherent response time of the sensor [15].

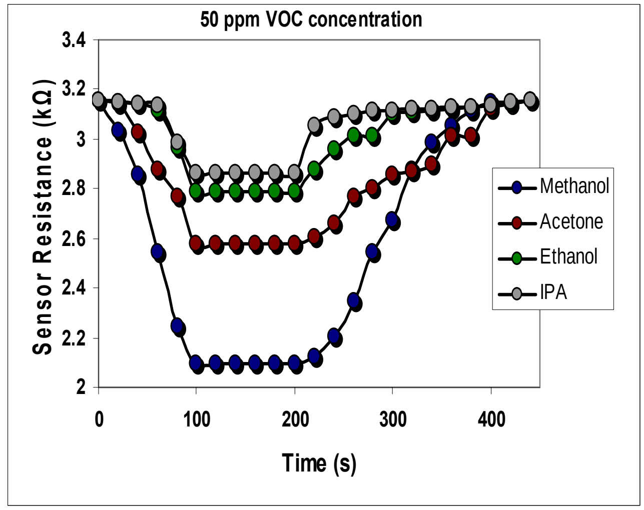


Figure 9. Response of the sensor to different VOCs at 50 °C operating temperature.

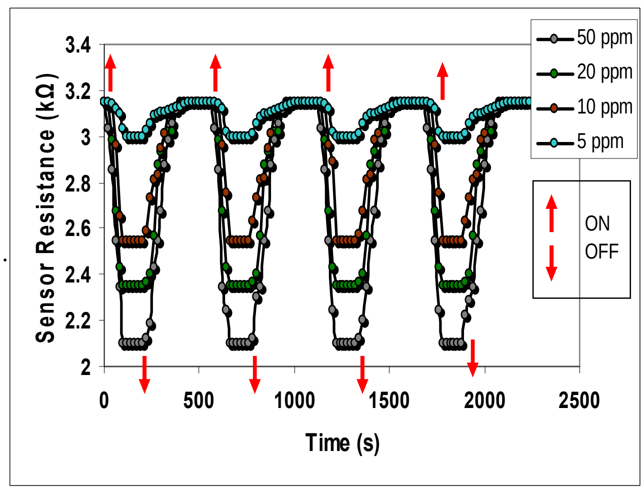


Figure 10. Dynamic response of the sensor for different concentration of methanol vapors at operating temperature of 50 °C. The arrows indicate the switching ON and OFF of N_2 flowing through the bubbler containing methanol.

From these studies, it can be inferred that, if at a given time, several VOCs are present, then the sensor developed in the present work cannot distinguish these individually. However, one can use this sensor in application such as electronic nose where there is an array of sensitive sensors and the response can be given to artificial neural network for training and testing purpose. Identifying a particular VOC in presence of several other VOCs continues to be a challenge.

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IV. CONCLUSION

The aim of the present work was to develop energy efficient sensors, which are capable of operating at considerably reduced temperatures. For this purpose, nanostructured ZnO was synthesized using a catalyst-free process and the same was integrated with MEMS processing. To reduce the power consumption of the microheater integrated with the sensor, an innovative technique for fabricating the sensors on a planar and thermally isolated MEMS platform is presented. It has been demonstrated that the fabricated sensors are energy-efficient. The sensor is prepared using low cost materials and is capable of detecting methanol vapors at 50 °C utilizing only 40 mW of power. The sensor showed quite a large change in its resistance on exposure to methanol at 50 °C. The concept of a thermally isolated oxide platform is implemented using technologies which are standard processes in integrated circuit and MEMS manufacturing. The mechanical strength of the silicon substrate is not compromised in the present technology, as is the case when similar levels of power reduction is achieved by creating a cavity by partial etching of silicon from the back side or making a sensor on a suspended diaphragm. The standard packaging techniques can be used for the innovative sensors developed in the present work as the silicon wafer has no cavities in it. The proposed process does not require any modification in mask design, wnen the substrate thickness changes because of wafers of different diameter. Double-side polished wafer is also not needed in the present work. The issues of compatibility of sensing layer material with etchants used for the formation of sensing electrode of aluminum are completely resolved by using lift-off process for patterning the Zn film.

ACKNOWLEDGEMENT

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An Indian Patent application (1802/DEL/2012 dated 12 June 2012) has been filed covering some of the innovations presented here.

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