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A hybrid YSZ/SnO₂/MEMS SO₂ gas sensorTing-Jen Hsueh^a and Chun-Liang Lu^b

This study uses a solid YSZ electrolyte film in a SnO₂ MEMS SO₂ gas sensor of the semiconductor type to enhance the redox reaction. The YSZ film is prepared by RF sputtering. XRD analysis shows the presence of the (111), (200), (220) and (311) peaks that denote the crystallization planes of YSZ. The experimental results show that the SnO₂ MEMS SO₂ gas sensor with a YSZ film has a better sensor response than a pure SnO₂ MEMS SO₂ gas sensor or a YSZ MEMS SO₂ gas sensor when the SO₂ concentration and the sensor's temperature sensors are 250 ppb and 400 °C, respectively. The YSZ/SnO₂ sensor's measured responses are around 6%, 45%, 20% and 16% when the sensor is respectively operated at 250 °C, 300 °C, 350 °C, and 400 °C.

Introduction

As technological advances and industrial development are becoming more rapid in the petrochemical industry, environmental pollution has become an important issue. The types of air pollutants include nitrogen oxides (NO_x), sulfur oxides (SO_x) and PM2.5 (particulate matter with a diameter of 2.5 μm or less).¹ SO_x causes acid rain, soil acidification and climate change.² SO_x become PM2.5 when molecules of SO_x react with basic compounds in the atmosphere.^{2,3} In the family of SO_x (such as SO, SO₂, SO₃ etc.), sulfur dioxide (SO₂) is a major component, and is usually the indicator that is used for SO_x monitoring.⁴ SO₂ is one of the most toxic substances known. It is known that toxic gases are hazardous to human health.

Over the past decade, toxic gases have been detected using electrochemical, catalytic bead, photoionization, infrared point and semiconductor devices. The electrochemical type can be divided into those that use liquid electrolytes or solid-state electrolytes. Solid electrolytes are widely studied because they are accurate and reliable, small and light, flexible to install and easy to use.⁵ Yttria stabilized zirconia (YSZ) devices have high chemical and thermo mechanical stability.⁶ For thick film applications, the operating temperature of the YSZ is more than 600 °C.⁶

Recently, the authors reported a SnO₂ micro-electro mechanical systems (MEMS) gas sensor.⁷ Semiconducting metal oxide MEMS gas sensors have a number of advantages in terms of use in consumer devices, such as low cost, high efficiency, high integration, low power consumption, high sensitivity and being well suited to wearable applications. They are

potentially compatible with silicon microelectronics. The oxygen-related gas-sensing mechanism involves the absorption of oxygen molecules on the oxide surface to generate chemisorbed oxygen species (O₂⁻, O²⁻, O⁻) by capturing electrons from the conductance band, which makes the oxide surface highly resistive. The oxide is exposed to traces of the reductive gas. In reacting with the oxygen species at the oxide surface, the reductive gas reduces the concentration of the oxygen species on this surface and thereby increases the electron concentration.⁸ However, SO₂ molecules have an indistinctive redox reaction.³

To sense SO₂ molecules and to increase energy savings, this study uses a solid electrolyte YSZ film in a SnO₂ MEMS structure to form a MEMS SO₂ gas sensor. The properties of the fabricated sensors are also determined. The sensing properties of the YSZ thin film SO₂ gas sensor are determined.

Experimental

Fig. 1(a) schematically depicts the processing steps for the YSZ/SnO₂ MEMS SO₂ gas sensor and Fig. 1(b) shows the structure of the YSZ/SnO₂ MEMS SO₂ gas sensor. The structure comprises a suspension, an isolation layer, a micro heater and a sensing material. The micro heater provides a heat source that generates temperatures up to 450 °C. Recently, the authors reported the fabrication of a MEMS SO₂ gas sensor structure.⁹ This study uses a different micro heater material, interdigital transducer (IDT) electrode (Ni/Cr) and sensing film (YSZ/SnO₂). Prior to the fabrication of an YSZ/SnO₂ MEMS SO₂ gas sensor, a 6 inch Si wafer was thermally oxidized to form a 700 nm-thick SiO₂ film. Standard photolithography was used to define the micro heater and the IDT electrode and a 50 nm thick Cr adhesion layer was deposited on a SiO₂/Si substrate. A 300 nm Ni film was then deposited on the Cr/SiO₂/Si substrate using electron

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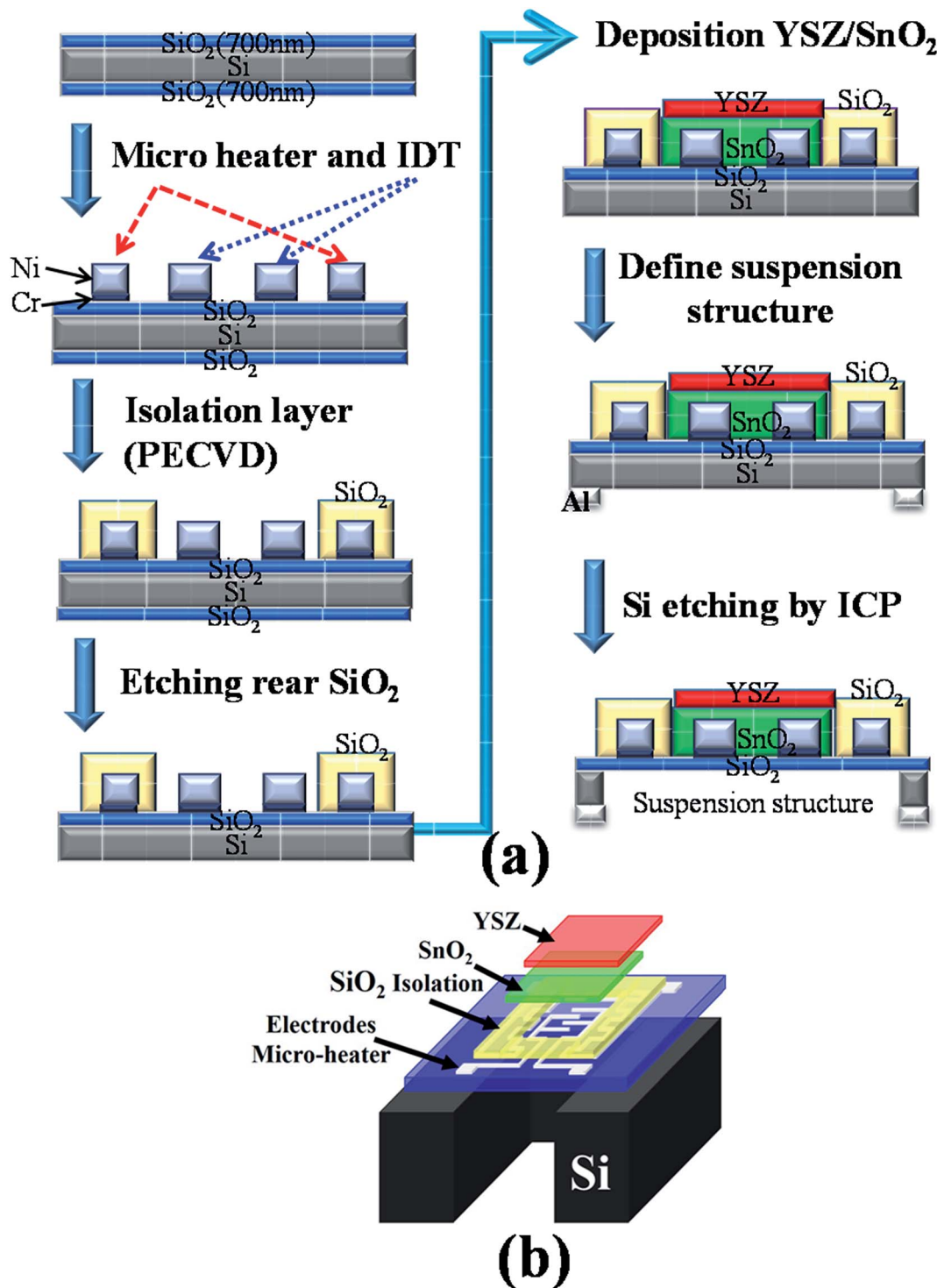


Fig. 1 (a) A schematic diagram of the processing steps for the YSZ/SnO₂ MEMS SO₂ gas sensor and (b) the structure of the YSZ/SnO₂ MEMS SO₂ gas sensor.

gun evaporation. A 400 nm SiO₂ was deposited on the micro heater using PECVD.

For the sensor film, a 600 nm thick SnO₂ layer and a 300 nm thick YSZ layer were deposited by sputtering. Acetone was used to remove the positive type photoresist.

Finally, on the reverse side, a 200 nm thick Al layer was then deposited as the etching barrier layer by sputtering. Standard photolithography was used to make a mask to etch the Al layer. Acetone was used to remove the positive-type photoresist and the exposed Al was then wet-etched using



aluminum etch. For the DRIE process, the flow rates for SF_6 gas and O_2 gas, the substrate temperature, the etching time, the electrode gap, the RF power and the chamber pressure were set at 6.3 sccm, 70 sccm, -120°C , 210 min, 7 cm, 1000 W, and 10 mTorr, respectively.

The thermal image and morphology were measured using a thermal imaging camera and field-emission scanning electron microscopy (FESEM, JEOL JSM-7000F). The crystallographic properties of the as-grown samples were then determined using X-ray diffraction (XRD; MXP18, and MAC Science) measurements. The resulting gas sensor was then electronically characterized using a Keithley 2400 source meter and a personal computer.

Results and discussion

Fig. 2(a) shows the top view SEM images of the YSZ/ SnO_2 MEMS SO_2 gas sensor. It is found that the morphology of the surface is the same as that in Fig. 1(b). Fig. 2(b) shows the top optical microscopy image of the YSZ/ SnO_2 MEMS SO_2 gas sensor. It was found that the annular micro-heater surrounds the finger-like

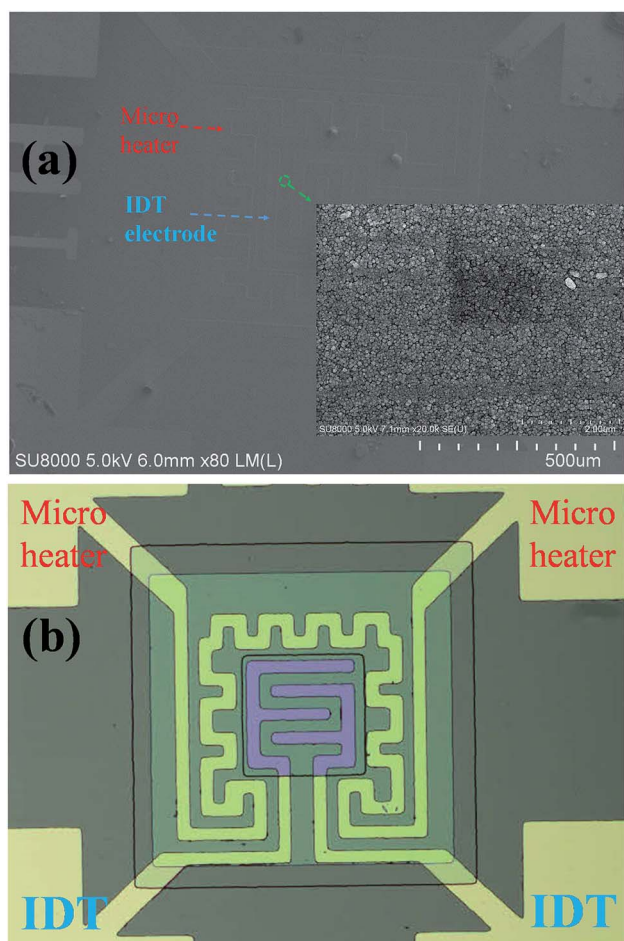


Fig. 2 (a) The top view SEM images of the YSZ/ SnO_2 MEMS SO_2 gas sensor. The inset shows an enlarged image of the sensing film (green dotted circle). (b) The top optical microscopy image of the YSZ/ SnO_2 MEMS SO_2 gas sensor.

electrodes. The inset of Fig. 2(a) shows an enlarged image of the sensing film (green dotted circle). It is seen that the YSZ has a uniform grain size, with a diameter of about 50 nm. It is also seen that there is a gap between each grain of at most 20 nm. These interfaces create oxygen diffusion pathways for gas sensing.¹⁰

Fig. 3 shows the crystalline properties of YSZ films from their XRD patterns. YSZ films were deposited on a $\text{SnO}_2/\text{SiO}_2/\text{Si}$ substrate using the sputtering parameters, without thermal treatment. The (111), (200), (220), and (311) peaks denote the crystallization planes of YSZ (JCPDS 30-1468). The (111) is the main growth plane.

A resistive heater operates on the metal wire thermal principle. Fig. 4(a) shows infrared thermal images of the YSZ/ SnO_2 gas sensor. There is a temperature difference between the micro heater (red square) and the suspension structure (red dashed lines). The other area is also approximately at room temperature because the micro heater provides a heat source and the suspension structure prevents thermal diffusion. The temperature of the sensing film is approximately 201°C , 251°C , 297°C , 350.6°C and 400°C when the current in the micro-heater is approximately 33 mA, 37 mA, 39 mA, 42 mA and 44 mA, respectively, as shown in Fig. 4(b). The current increase linearly as the temperature is increased. When the temperature of the sensing film is 201°C , 251°C , 297°C , 350.6°C , and 400°C , the required power is 103 mW, 136 mW, 164 mW, 197 mW, and 229 mW, respectively.

Fig. 5 shows the detector sensor responses for three SO_2 gas sensors, measured at 400°C . During these measurements, 250 ppb SO_2 gas was introduced into a sealed chamber and the resistivity of the sensor was measured in air (R_a) and in the presence of SO_2 gas (R_b). To quantify the sensor's performance, the response of this sensor is $[(R_a - R_b)/R_a] \times 100\%$.¹¹ This definition gives a sensor response of 16% for the YSZ/ SnO_2 sensing film with the MEMS structure (micro-heater and

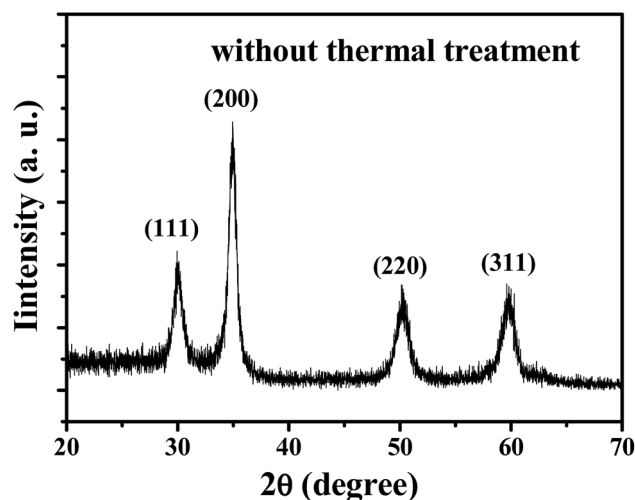


Fig. 3 The XRD patterns for YSZ films: YSZ films were deposited on a $\text{SnO}_2/\text{SiO}_2/\text{Si}$ substrate.



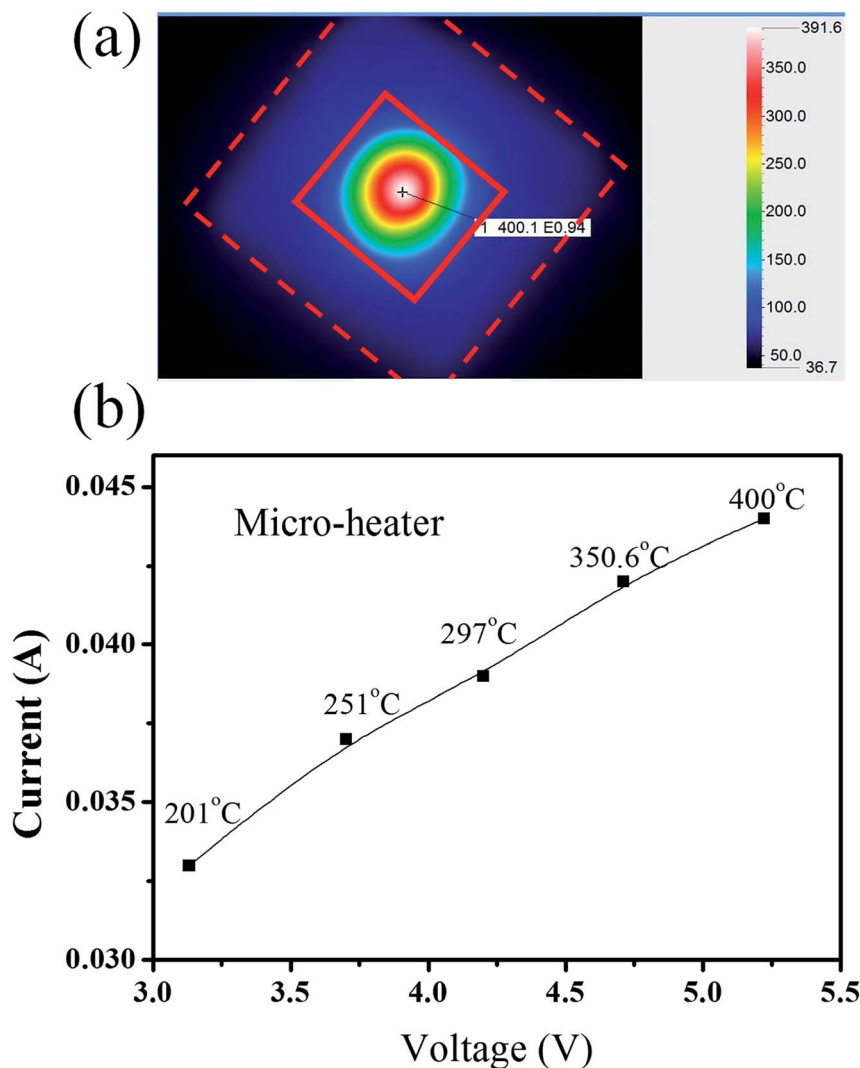


Fig. 4 (a) Infrared thermal images of the YSZ/SnO₂ gas sensor and (b) the temperature of the sensing film.

suspending structure). The sensor response is only around 10% for the pure SnO₂ thin film. In other words, the sensitivity to SO₂ gas is significantly increased by the deposition of YSZ

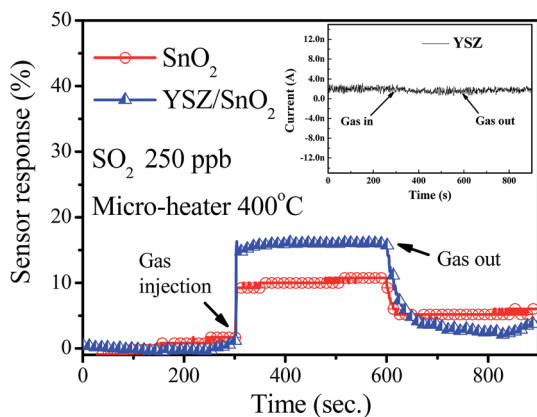


Fig. 5 Detector sensor responses for various SO₂ gas sensors, measured at 400 °C. The inset in Fig. 4 shows that the sensor response for the sample with only the YSZ film.

film on the SnO₂ thin film surface. A sample with only the YSZ thin film was prepared and the same SO₂ gas sensing measurement at 400 °C was performed. The inset in Fig. 5 shows that the sensor response for the sample with only the YSZ film is a null response. This result shows that the large 16% sensor response is attributable to the SnO₂ thin film with YSZ film (YSZ/SnO₂). It has been reported that the SnO₂ can be used to sense toxic gas with low sensitivity at higher temperatures.^{10,12} In terms of the sensing mechanism for a YSZ/SnO₂/MEMS SO₂ sensor, the YSZ thin film allows the redox reaction and the SnO₂ thin film acts as an electronic transmission path. As shown in Fig. 6(a), when the YSZ/SnO₂/MEMS SO₂ sensor is surrounded by air, oxygen molecules are adsorbed onto the YSZ surface and capture electrons from the sensing thin film to generate chemisorbed oxygen species (O₂⁻, O²⁻, O⁻). Therefore, the sensor becomes highly resistive. When SO₂ gas is introduced, the sensor is exposed to traces of reductive gas. The reductive gas reacts with the oxygen species on the YSZ surface and the concentration of oxygen species on the YSZ surface is reduced, so the concentration of electrons is



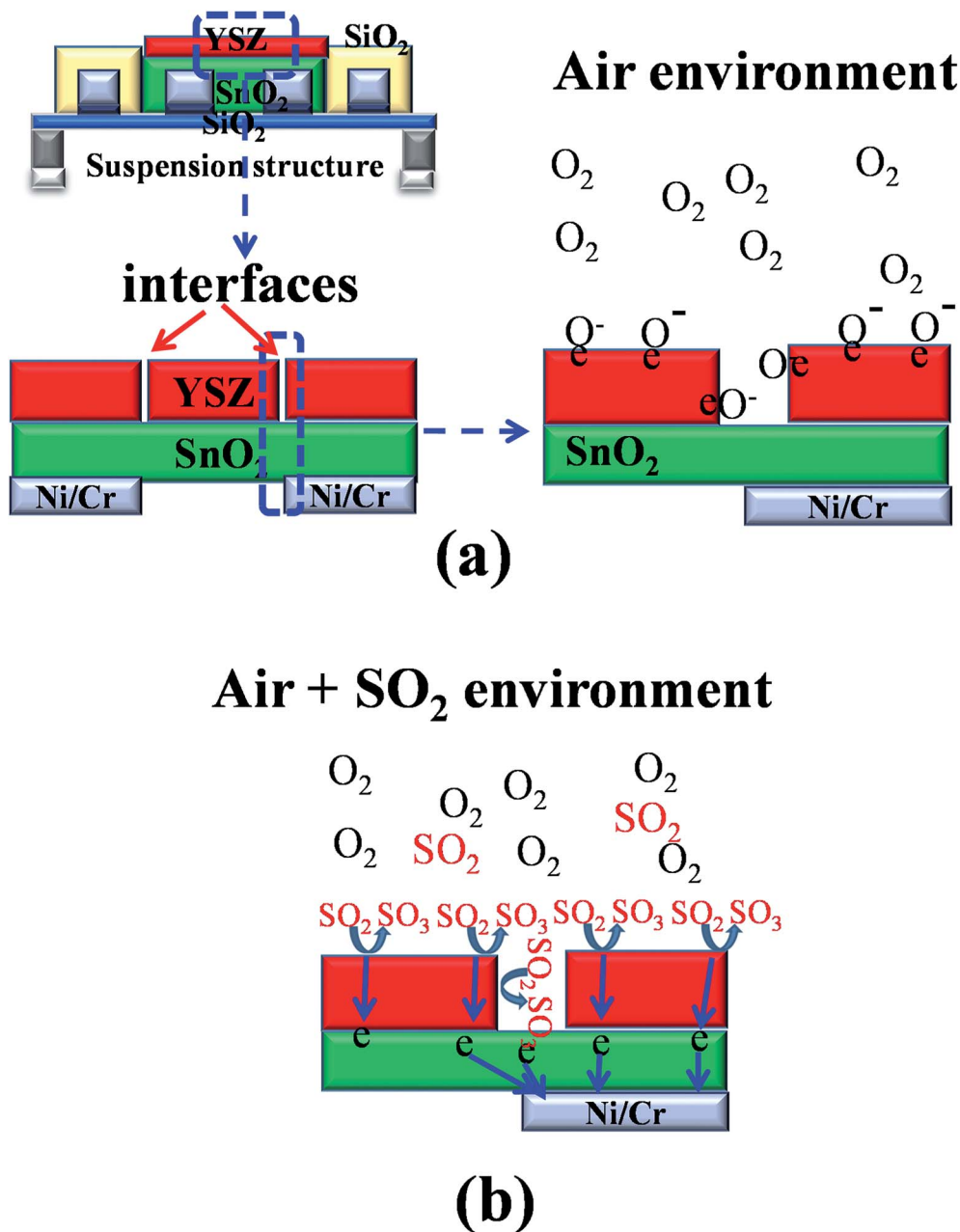


Fig. 6 Schematic diagram of a YSZ/SnO₂/MEMS SO₂ sensor surrounded by (a) air and (b) SO₂ gas.

increased, as shown in Fig. 6(b) and the sensor becomes more conductive.

Fig. 7 shows the sensor response of the YSZ/SnO₂/MEMS sensor measurement various gases at 400 °C. It was found that the measured response is around 16% and 6% when the concentration of injected SO₂ and H₂S gas is 250 ppb, respectively. It also was found that the sensor response of YSZ/SnO₂/MEMS sensor is not obvious when the concentration of NH₃ and NO₂ gases are 250 ppb, respectively. The measured results was shown that the YSZ/SnO₂/MEMS sensor is more responsive to sulfide; especially SO₂ gas.¹⁰

Fig. 8 shows the variation in sensor response variations for a YSZ/SnO₂/MEMS SO₂ sensor when it is exposed to pumped

SO₂ gas. These measurements were performed by injecting various amounts of SO₂ gas into the sealed chamber, followed by pumping at 400 °C (micro-heater). Using the same definition, the measured response is around 16%, 23%, 27% and 31% when the concentration of injected SO₂ gas is 250 ppb, 500 ppb, 750 ppb and 1000 ppb, respectively. In other words, the sensor response increases when the SO₂ gas concentration increases. The measured device resistivity also responds rapidly when SO₂ is injected gas into the chamber and pumped away. This result shows that the fabricated sensor responds rapidly.

Fig. 9(a) shows the sensor response for the YSZ/SnO₂ sensor at various temperatures. It should be noted that only 250 ppb



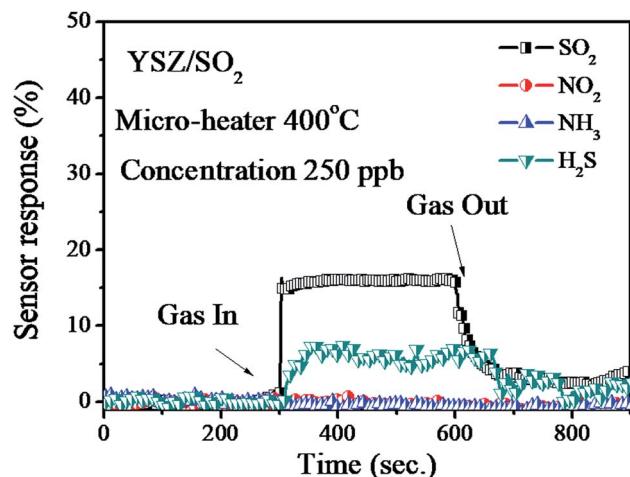


Fig. 7 The sensor response for the YSZ/SnO₂/MEMS sensor to various gases at 400 °C.

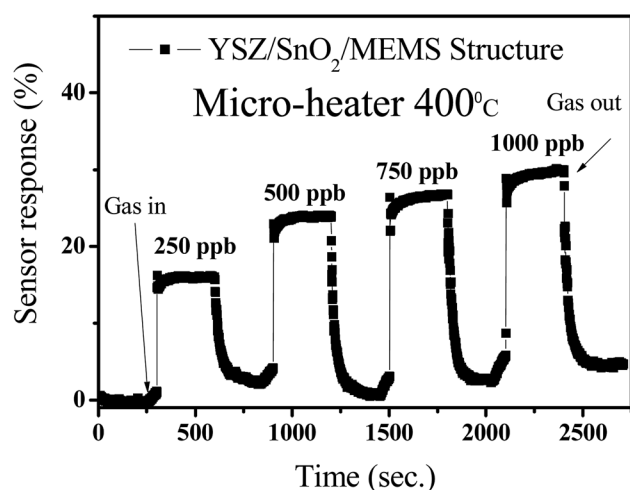


Fig. 8 The variation in sensor response for the YSZ/SnO₂/MEMS sensor material when SO₂ gas is injected and pumped.

SO₂ gas was injected into the chamber for these measurements. The measured responses are around 6%, 45%, 20% and 16% when the sensor is operated at 250 °C, 300 °C, 350 °C and 400 °C, respectively. In other words, sensor response increases initially, reaches a maximum at 300 °C and then begins to decrease as the operational temperature is increased from 250 to 400 °C. At low temperatures, the poor sensor response is attributed to the fact that SO₂ molecules do not have enough thermal energy to react with the surface-adsorbed oxygen species. However, the reduction in sensor response above 300 °C is attributed to the difficulty of exothermic SO₂ gas adsorption.¹¹ This result is similar to that of the study by Duan *et al.*¹³ To verify the reproducibility of the YSZ/SnO₂/MEMS SO₂ sensors, three good samples were randomly produced using the same wafer, as shown in Fig. 9(b). It is seen that the results are reproducible with an inaccuracy of $\pm 5\%$. These values show that the sensor that is proposed by this study has many applications.

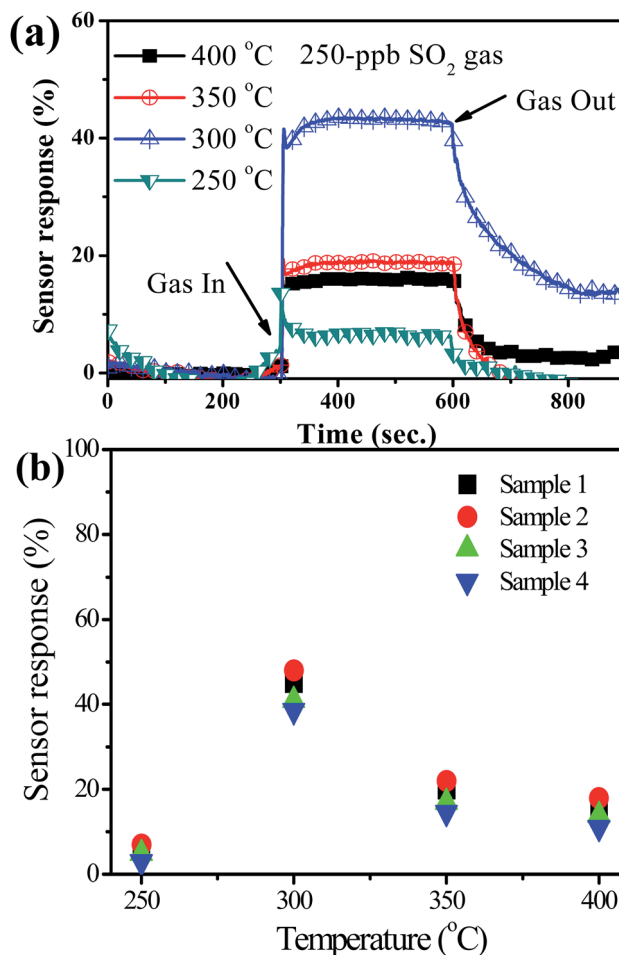


Fig. 9 (a) Sensor response for the YSZ/SnO₂ sensor at various temperatures and. (b) Five of the same samples at various temperatures (including the sensor of (a)).

Conclusion

In summary, YSZ film is deposited by RF sputtering into a SnO₂ MEMS SO₂ gas sensor to form a YSZ/SnO₂ MEMS SO₂ gas sensor. XRD analysis shows the presence of (111), (200), (220), and (311) peaks that denote the crystallization planes of YSZ. Compared with a SnO₂ MEMS SO₂ gas sensor and a YSZ MEMS SO₂ gas sensor, a YSZ/SnO₂ MEMS SO₂ gas sensor has the best sensor response when the sensors are at 400 °C and in 250 ppb SO₂ gas ambience. The measured responses for the YSZ/SnO₂ sensor are also around 6%, 45%, 20% and 16% when the sensor is operated at 250 °C, 300 °C, 350 °C and 400 °C, respectively.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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