Micromachined catalytic combustion type gas sensor for hydrogen detection

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A catalytic combustion hydrogen sensor has been fabricated using the microelectromechanical system technology. The application of hafnium oxide thin films as the insulating layer has been deposited by electron beam evaporation. The semiconductor combustion catalyst tin oxide layer was prepared by chemical vapour deposition. It is a novel application of semiconductor material to a catalytic combustion gas sensor. The resistivity of hafnium dioxide thin film is about 3×10^{12} Ω cm at 900°C. Both the sensing elements and the reference elements could be connected in a suitable circuit such as a Wheatstone configuration with low power consumption. The catalytic combustion sensor shows high response to hydrogen at an operating voltage of 4 V and has a higher relative sensitivity and a good linearity for concentrations of hydrogen ranging from 0 to 4% in volume. Good consistency and high accuracy of the micromachined catalytic combustion gas sensor were achieved.

1. Introduction: Hydrogen is a very dangerous gas because it will be explosively flammable when mixed with air at a very wide range of concentrations between 4 and 75%. To avoid hydrogen explosion accidents, research to achieve a hydrogen catalytic sensor which is fast, has wide range and high sensitivity is of great significance. Catalytic combustion gas sensors have been widely used for many years to detect flammable gases because of their simple structure, low cost, good stability and anti-poisoning properties. In the traditional catalytic combustion gas sensor, the porous catalyst adhered on a platinum coil, which is employed as heater and thermistor simultaneously. The resistance of the catalyst layer influenced the veracity of the thermistor. Therefore only a few kinds of insulating materials are selected as the catalyst carrier. Many transition metal compounds cannot be used as the catalyst or the catalyst carrier because of their semiconductor nature. With the development of microelectromechanical system (MEMS) technology, silicon micromachining has been used to manufacture modern catalytic combustion gas sensors on silicon substrate with thin film deposition. In a typical micromachined catalytic combustion gas sensor, the insulating layer is SiNx, which is deposited between the microheater and the catalysts [1, 2]. However, it is found that the insulating property of SiNx is not stable when the temperature increases. It will affect the stability and the sensitivity of the sensor, especially at high concentration H_2. When the concentration of H_2 is greater than 1%, the temperature of the inner part of the sensor element will increase quickly up to 800°C. Silicon nitride has conductivity at high temperature. The decline of the insulating capability will limit the range of detection of hydrogen, usually lower than 1%vol. If there is a layer with stable insulating properties at high temperature on top of the heater, it will broaden the range of detection of hydrogen. Hafnium dioxide (HfO_2) thin film has attracted much attention in recent years for its outstanding chemical and thermal stability [3, 4]. The HfO_2 thin film has been applied as insulating material in the furnace because of its insulating property at high temperature and also has been used as anti-oxidation and antireflective films on the diamond surface to meet the need of the high-temperature environment (about 900°C) [5]. It is a promising dielectric material as a substitute for the conventional material as the insulating layer in combustion gas sensors.

In this Letter, a new type of microcatalytic combustion gas sensor system was designed and fabricated using MEMS technology. A unique material hafnium oxide had been deposited by electron beam evaporation as the insulating layer. A nanostructured catalyst tin oxide (SnO_2) was prepared by chemical vapour deposition (CVD). High sensitivity, good linearity to hydrogen in the range of 0–100%LEL (4%vol.) and lower total power consumption are expected when hafnium oxide is used as the insulating layer and nanostructured SnO_2 is used as catalyst in the sensor.

2. Experiment

Fabrication of catalytic combustion gas sensor: The micromachined catalytic combustion hydrogen gas sensor schematic is shown in Fig. 1. The sensor was fabricated with 270 µm-thick (100) double-sided polished silicon wafer using MEMS technology [6–8]. The Si wafer was cleaned by a standard wafer cleaning process. The top surface of the wafer was first coated with a 500 nm-thick layer of thermal oxide designed to help minimise any residual stress in the final microhotplate membrane. A 300 nm-thick layer of low-stress silicon-rich silicon nitride (SiNx) was deposited by low-pressure CVD as the etch stop and standing layers after the thermal oxide. Then, a 200 nm-thick layer of platinum was deposited by the sputtering method, which was then patterned to form a microheater structure. The Pt microheater was fabricated by MEMS techniques. After spin-coating (AZ1500), photolithography, sputtering and lift-off processes, the meander design geometry of Pt is deposited at the specified location. A 10 nm-thick adhesion layer of tantalum is necessary

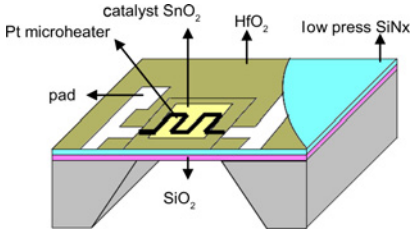

Figure 1 *Schematic of catalytic combustible hydrogen gas sensor*

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to improve the adhesion of the platinum film on the silicon nitride layer. A further 200 nm-thick layer of HfO_2 as insulating layer was deposited by electron beam evaporation (AXXIS™ thin film deposition systems, Kurt J. Lesker) with a base vacuum less than 6×10^{-7} Torr. An HfO_2 (99.99%) ceramic target was used as the evaporation source. On top of the insulating layer was a catalyst SnO_2 layer. The nanostructured SnO_2 was prepared using a novel CVD method at room temperature, and tin chloride anhydrate was used as the precursor. The experimental procedure is described as follows. The ammonia gas flew into the reactor. Then, $SnCl_4$ anhydrate was injected into the quartz reactor, and reacted with NH_3 to form $Sn(OH)_4$ nanospheres. A high-voltage electrostatic field was applied between the two electrodes using a bipolar power supply, and it bombarded the $Sn(OH)_4$ nanospheres onto the substrates. The resulting materials were washed with deionised water until the Cl^- ions were removed completely. Then, the substrates were subject to drying up at 80°C overnight and the $Sn(OH)_4$ nanospheres transformed to SnO_2 nanospheres. The SnO_2 nanospheres were annealed in air at 500°C. Then, SiO_2 and SiNx on the back of the device were removed by SF_6 and Si was finally back-etched anisotropically with 33% KOH solution at 80°C to create the thin membrane structure. The membrane area is 500×500 µm in the centre of the 1×1 mm silicon die. The microheater and insulating layer area are 250×250 µm and 300×300 µm, respectively. The Pt heater had a nominal resistance of 35 Ω.

3. Results and discussion

3.1. Characteristics of HfO_2 films: The stoichiometry of HfO_2 films has a great influence on the insulation properties. Therefore research on the stoichiometry of HfO_2 films is important. The chemical composition of HfO_2 films is determined by X-ray photoelectron spectroscopy (XPS). The XPS spectra for HfO_2 annealed at 500°C are shown as Fig. 2*a* Hf4f, and Fig. 2*b* O1s. The O/Hf ratio of HfO_2 films can be calculated from the Hf4f and O1s peaks using the following formula [9]

$$N_1{:}N_2 = A_1/S_1{:}A_2/S_2 \quad (1)$$

Here, A_1 and A_2 are the areas of the peaks corresponding to elements 1 and 2, respectively. S_1 and S_2 are the sensitive factors of elements 1 and 2, respectively.

Before calculating the ratio, it is important to distinguish between the O bound to HfO_2 and bound to other sources. Removing the contribution of the O bound to other sources from the total O, it is deduced from the results of XPS spectra of HfO_2 films that the chemical composition of this sample is 2.01, apparently close to the stoichiometry.

Fig. 2 shows the XPS spectra for Hf4f and O1s core levels. All the spectra are calibrated by setting the C1s peak at 284.5 eV to remove the charging-induced energy shift because of X-ray exposure. As shown in Fig. 2*a*, the binding energies of Hf4f7/2 and Hf4f5/2 are fixed at 16.8 and 18.4 eV, respectively, which have been assigned to be emitted from the Hf4+ ions in the HfO_2 structural configuration [10, 11]. It indicated that a certain portion of Hf atoms has been fully oxidised. These phenomena are in good agreement with the previous results of the ratio O/Hf. The O1s primary peak at 530.1 eV is attributed to the O–Hf binding in HfO_2, and a shoulder band near the 532.3 eV peak is most probably little O–Si bonding in SiO*x*, as shown in Fig. 2*b*. From Fig. 2, it can be seen that most of the Hf element generates HfO_2.

The smooth dielectrics surface plays a very important role for the insulating layer in the micromachined catalytic combustion sensor because it could improve the performance and stability of the devices. The very smooth thin film's surface is favourable for the fabrication of high-quality sensors. The surface roughness is a very important factor for HfO_2 applications as it signifies homogeneity and particle formation of the film. An atomic force microscope (AFM) was used to directly measure the surface profile of the HfO_2 film on silicon substrate. The root-mean-square (RMS) roughness of the surface profile obtained through two-dimensional (2D) and 3D images by the AFM are presented as Fig. 3. The RMS roughness of the entire scanned area was measured as low as 1.75 nm. The average roughness of the thin film is 1.38 nm. From the measured values, it was found that the HfO_2 films are uniform and significantly smooth.

To obtain the insulating properties of hafnium oxide thin film, platinum metal had been deposited on and under HfO_2 as a metal electrode through a shadow mask by sputtering. Platinum electrodes of wire were connected to the DC power supply and digital galvanometer. The sample was placed in the furnace. The $V-I$ characteristics of the thin film from room temperature to 900°C were measured and the film volume resistivity was calculated. The resistance is shown in Fig. 4. From this Figure, it can be seen that, although the resistance of the film decreased gradually with the increase of temperature, at a high temperature of 900°C (generally the highest temperature of the catalytic combustion sensors), the

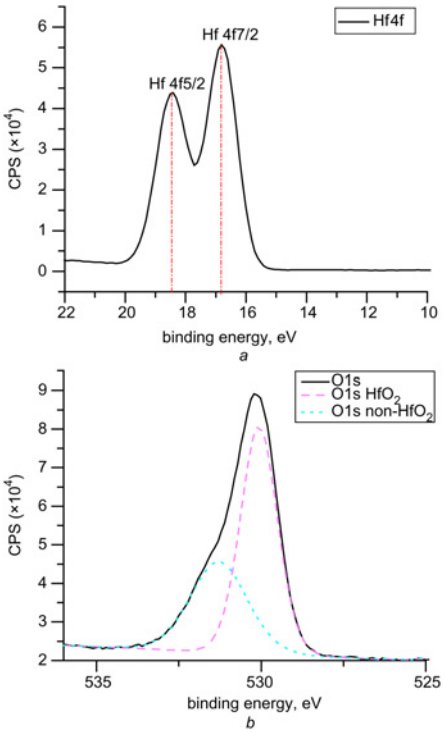

Figure 2 *XPS spectra of HfO_2 films*
a Hf4f
b O1s

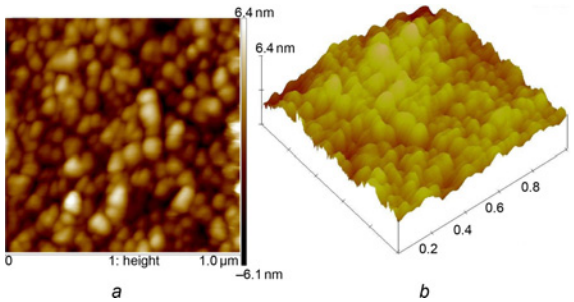

Figure 3 *AFM images of the HfO_2 thin films*
a Two-dimensional AFM image
b Three-dimensional AFM image

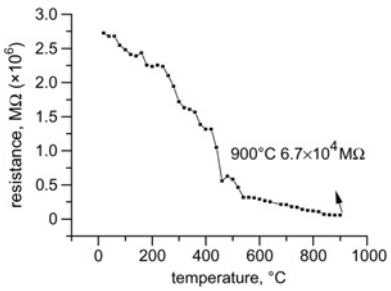

Figure 4 *Resistance of the HfO_2 thin film against test temperature*

resistance of the film is 6.7×10^4 MΩ, which means that the resistivity is up to 3×10^{12} Ω cm. Compared with the resistance of the heater, 112 Ω, the resistance of the HfO_2 layer is 10^8 times higher. At 900°C, the insulation of hafnium oxide is so good as to meet the requirements of insulation of the catalytic combustion sensor.

3.2. Structure and morphologies of SnO_2: The vapour phase deposition process was identified as a two-step reaction. First, $SnCl_4$ vapour reacted with ammonia gas to form $Sn(OH)_4$. Then, the intermediate products were dehydrated to form SnO_2 nanospheres. When the process was terminated before sintering at 500°C for 2 h, SnO_2 nanospheres could also be obtained. The reaction can be formulated as

$$SnCl_4 + 4NH_3 \cdot H_2O = Sn(OH)_4 + 4NH_4 \cdot Cl$$
$$Sn(OH)_4 = SnO_2 + 2H_2O$$

X-ray powder diffraction (XRD) was carried out to identify the crystalline phase of the as-prepared samples as shown in Fig. 5*a*. It could be observed that the products were crystals and all peaks could be well indexed according to the JCPDS Card No. 41-1445 powder diffraction database. The XRD of the SnO_2 revealed mainly peaks corresponding to the tetragonal rutile structure of SnO_2. From the X-ray diffraction data, it is concluded that the material has an incomplete crystallisation as-prepared and is strongly (101) oriented. After annealing at 500°C, it is pure phase SnO_2 and the diffraction peaks of (110), (211) crystal faces become clear. It is clear that the powders which are not annealed were not fully crystallised and those annealed at 500°C are well crystallised.

The morphology of SnO_2 nanostructures were characterised by scanning electron microscopy (SEM) (S-4800 SEM). Fig. 5*b* shows SEM images of SnO_2 catalyst samples: unannealed and annealed at 500°C, respectively. It is seen from the images that there are very fine uniformly nanospheres. The powder size from the films unannealed (about 120 nm) is larger than those annealed at 500°C (about 80 nm). Ammonium chloride generated in the first step is used as the pore of porous materials. The principle of the pore-forming agent is: some materials will produce chemical

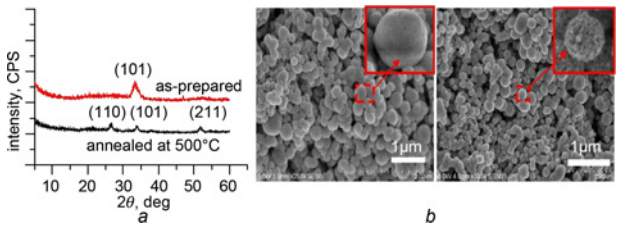

Figure 5 *Characteristics of the nanospheres SnO_2*
a XRD patterns
b SEM images

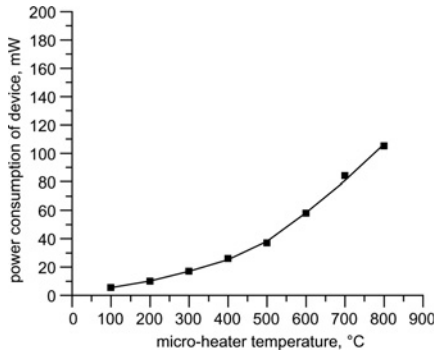

Figure 6 *Power consumption of the microhotplate at different operating temperatures*

reaction at high temperature. This leads to the change in the volume or quality. Ammonium chloride decomposes into ammonia and hydrogen chloride gas at high temperature. Hence, after high temperature treatment the size becomes more porous than those unannealed. The porous nature of spheres and the high surface to volume ratio of annealed nanoparticles would also enhance the effective surface area and enable the gas to react easily.

3.3. Characteristics of microheater: Changes of the platinum heater current were monitored when a linearly increasing voltage was applied to the heater. The power consumption of the device was then calculated based on the current. The microheater resistance is a one-to-one relationship with the temperature. The data of power consumption of the microheater at different operating temperatures were compiled and analysed for the device performance as shown in Fig. 6. From the slope of the curve, it is found that the rate of temperature increase on the heater is

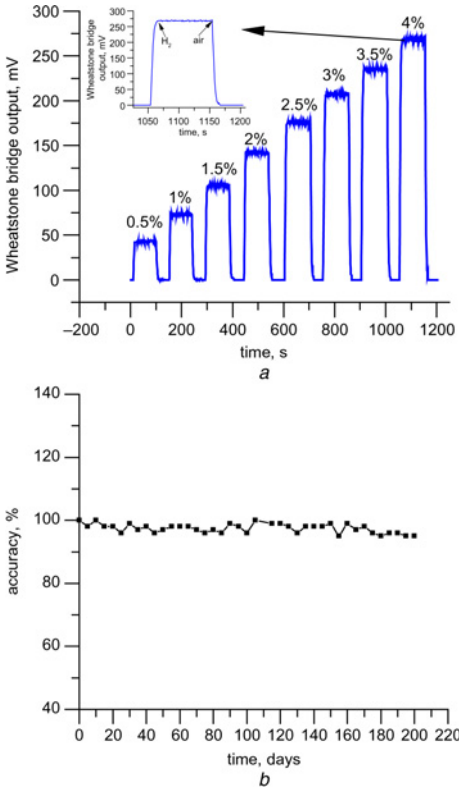

Figure 7 *Gas sensor response to various concentrations of hydrogen, and long-term stability of the gas sensor*
a Gas sensor response
b Long-term stability

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Table 1 Accuracy and reproducibility of gas sensors 1, 2, 3

v/v, %	1, mV	2, mV	3, mV	AVG, mV	RSD, %
0.5	37.6	39.0	42.0	39.5	5.7
1.0	66.2	65.1	70.4	67.2	4.6
1.5	106.3	105.8	108.8	107.0	1.5
2.0	135.5	135.6	140.2	137.1	2.0
2.5	168.2	164.2	170.8	167.7	2.0
3.0	190.1	201.9	200.3	197.4	3.2
3.5	220.8	220.0	225.6	222.1	1.4
4.0	256.3	260.2	262.0	259.5	1.1

13°C/mW at 300–500°C. The power consumption of the microhotplate is 37 mW at 500°C.

3.4. Response to hydrogen: The micromachined gas sensors were connected in one arm of a Wheatstone bridge. It consists of two parts, a sensing element and a compensator element. For the sensor, catalytic combustion of H_2 is obtained by electrically heating the catalyst material to the required temperature with the platinum heater. The responses to various concentrations of hydrogen varying between 0 and 4% at 4 V of applied driving voltage are shown in Fig. 7*a*. The output voltages of the Wheatstone bridge are proportional to hydrogen concentrations. The sensitivity to 1% hydrogen was 67 mV. Compared with the traditional catalytic combustion gas sensor (sensitivity 40 mV/1% H_2), this method has a higher relative sensitivity and a good linearity for the concentration of hydrogen ranging from 0 to 4%. The response of the sensor to 4% hydrogen is shown in Fig. 7*a*. The response time and recovery time were as short as about 6 and 7 s, respectively. The stability test was conducted and the sensor signal was very stable during 200 days (veracity >95%) (Fig. 7*b*).

The accuracy and reproducibility of the micromachined gas sensors were studied. As shown in Table 1, we prepared three sensors independently to detect the same hydrogen. Relative standard deviations of <6% were achieved. It indicated that this gas sensor has good reproducibility and high accuracy.

4. Conclusion: A novel application of HfO_2 films as the insulating layer in combustion gas sensors fabricated for H_2 measurement in the range of 0–4% is demonstrated in this Letter. The resistivity of the HfO_2 thin film deposited by electron beam evaporation is up to 3×10^{12} Ω cm, which demonstrates that these films can be deposited onto combustion gas sensors chips with a high degree of controllability and exhibit excellent insulating stabilities at high temperature. SnO_2 nanospheres were successfully synthesised by chemical vapour deposition using tin chloride anhydrate as the source material. The post-annealing at 500°C shows that at high annealing temperatures, a body centred tetragonal rutile crystalline structures of SnO_2 nanospheres is formed. The gas sensing characteristics of the micromachined gas sensors deposited SnO_2 films were measured using hydrogen as the test gas. Compared to the traditional catalytic combustion gas sensors, the sensor with HfO_2 as the insulating layer and SnO_2 nanospheres as catalyst has a higher relative sensitivity and a good linearity for the concentration of H_2 ranging from 0 to 4%. the response time is about 6 s and recovery time is about 7 s. Good consistency and high accuracy were achieved. Finally, the sensor signal was very stable during the long-term operation (veracity >95%).

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