Formaldehyde gas sensor based on TiO_2 thin membrane integrated with nano silicon structure*

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An innovative formaldehyde gas sensor based on thin membrane type metal oxide of TiO_2 layer was designed and fabricated. This sensor under ultraviolet (UV) light emitting diode (LED) illumination exhibits a higher response to formaldehyde than that without UV illumination at low temperature. The sensitivities of the sensor under steady working condition were calculated for different gas concentrations. The sensitivity to formaldehyde of 7.14 mg/m^3 is about 15.91 under UV illumination with response time of 580 s and recovery time of 500 s. The device was fabricated through micro-electro-mechanical system (MEMS) processing technology. First, plasma immersion ion implantation (PIII) was adopted to form black polysilicon, then a nanoscale TiO_2 membrane with thickness of 53 nm was deposited by DC reactive magnetron sputtering to obtain the sensing layer. By such fabrication approaches, the nanoscale polysilicon presents continuous rough surface with thickness of 50 nm, which could improve the porosity of the sensing membrane. The fabrication process can be mass-produced for the MEMS process compatibility.

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The metal oxide gas sensors operated at high temperatures up to 300 °C will lead to high power consumption, flammable gases ignition, growth of the oxide grain, and the long-term drift problems. So, some strategies, such as micro-electro-mechanical system (MEMS) fabrication, nanosensing materials and ultraviolet (UV) illumination, have been used to lower operating temperature, even at room temperature[1]. A way to make a sensor sensitive and recover fast for gas sensing is under UV light activation by low temperature heating[2]. Although the crystal of TiO_2 thin membrane was determined to be anatase phase in Ref.[2], the preparation technology was relatively complex and the thickness of thin film was difficult to control, moreover, the ball milling technique can't guarantee the homogeneity of the TiO_2 thin membrane grains. With respect to other aspects, the hollow TiO_2 microspheres can be prepared by mixing $Ti(OBu)_4$ and 0.1 g carbon microsphere[3], and TiO_2 membrane nanotubes can be prepared by anodization method[4]. The morphology of microsphere and nanotubes can be obtained by above two chemical methods of TiO_2 thin membrane preparation. The large surface area of the membrane will increase the contact area between the gas and sensitive film, and the sensitivity of the sensor is improved accordingly, but the production method is relatively complicated and can't be combined with MEMS process successfully. Although the thin membrane gas sensor can be mass-produced and both the thickness of the film and the size of the grain can be controlled, the high-density membrane is so compact that the gas is difficult to enter the sensitive membrane[5]. So the sensitivity of the thin membrane gas sensor is lower than that of the thick membrane type.

This paper has carried out the research with respect to a new integrated nanostructure planar diaphragm metal oxide formaldehyde gas sensor which can be mass-produced. The devices were produced by MEMS fabrication

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craft, meanwhile the operating temperature can be reduced to enlarge the application range and improve security through the illumination of low-power UV light emitting diode (LED). The nano-silicon integrated by MEMS fabrication craft can increase the contact area between the gas and sensitive film and enhance the utilization of UV light, so that the gas sensitivity can be improved. Therefore, it's very effective to construct black polysilicon by plasma immersion ion implantation (PIII) technology proposed in this paper, so as to increase the porosity of the thin membrane and enhance the gas sensitivity of the sensor.

The metal oxide gas sensor was fabricated by micromachining technology, and the micro-hotplate is a suspended structure which contains a heating element. It can be manufactured by a standard commercial complementary metal oxide semiconductor (CMOS) process and a polysilicon layer was used as the resistor-heating element. The small size of the micro-hotplate allows it to have a low thermal time constant. Before using PIII to form black polysilicon, the sensing Pt electrodes were prepared by lift-off photolithography and subsequent deposition of a 30-nm thick Pt layer by DC magnetron sputtering (Fig.1(c)).

Then, the black polysilicon was prepared by PIII process on home-made equipment. O_2 and SF_6 gases with the flow rates of 100 cm^3/min and 50 cm^3/min[6], respectively were inlet into the vacuum chamber. The radio frequency power of 900 W was matched to generate plasma and the working pressure was 0.86 Pa. 500 V negative voltage pulses were applied to the sample stage during the PIII process for 500 s (Fig.1(d))[6].

After that, use hard mask to make the TiO_2 membranes deposited in the area of black polysilicon by DC reactive magnetron sputtering (Fig.1(e)), from pure titanium target (99.95% purity) in a mixed Ar (99.999% purity) and O_2 (99.95% purity) atmosphere. Before deposition, the chamber was evacuated down to 5×10^{-4} Pa. The gas flow rates were regulated by the mass flow controllers and held constant at 15 cm^3/min and 10 cm^3/min for Ar and O_2, respectively. The partial pressure of oxygen measured before the start of the deposition was 0.11 Pa, the total pressure during the deposition was 0.24 Pa and the sputtering power was 150 W. In order to increase the crystallinity and to improve the long-term stability of the layers, the as-deposited films were annealed in ambient air at 600 °C for 1 h.

As silicon is a good heat conductor, it must be removed from the micro-hotplate to achieve high thermal efficiency. The localized removal of silicon from desired places was accomplished by using bulk micromachining techniques. XeF_2 can be used as a silicon etchant in this post-CMOS process (Fig.1(f))[5]. Then, the final gas sensor was realized. Fig.2(a) shows the 3D model of gas sensor with black polysilicon formed by PIII. Fig.2(b) shows the 3D model of the final gas sensor.

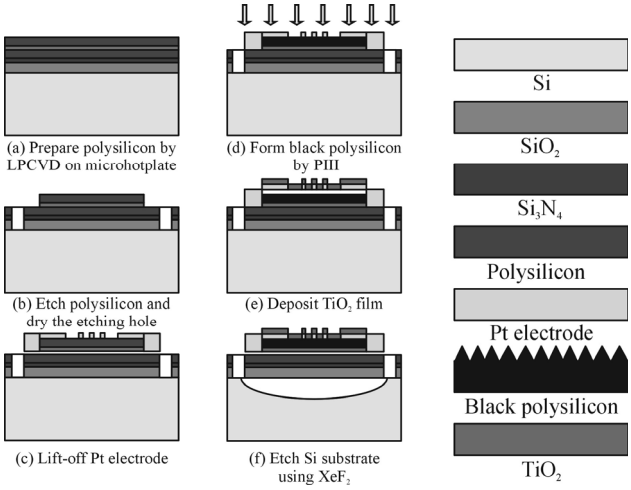
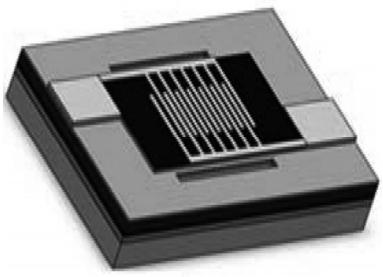


Fig.1 Fabrication process of the proposed gas sensor



(a) The gas sensor with black polysilicon formed by PIII

(b) The final gas sensor

Fig.2 3D model of the fabricated gas sensor

Obviously, the gas flux ratio of SF_6 to O_2 plays an important role in the microstructure and properties. When the content of SF_6 is relatively high, the surface would be smooth and the plasma would have an obvious effect on the etching of polysilicon. Conversely, there would be an uneven porous morphology on the surface. At present, when the optimal ratio of SF_6 to O_2 is 2.0, there would be continuous peaks on the surface of black polysilicon according to the experimental results. After 300 s, the average height of the peaks is about 20 nm. When we used the optimal ratio of SF_6 to O_2 to etch polysilicon for 500 s, we can get the expected structure which is depicted in Fig.3[7-9]. Scanning electron microscope (SEM) images of the surface morphology of the TiO_2 nanoparticles are shown in Fig.4(a) and (b). The average diameter of crystalline grains is about 10 nm and the nanoscale TiO_2 membranes are about 50 nm thick.

The TiO_2 phase has been further confirmed by Raman analysis. Referencing undoped TiO_2 crystal Raman spectra data, the anatase phases corresponding to the Raman spectral peaks are 515 cm^{-1}, 147 cm^{-1}, 399 cm^{-1}, 198 cm^{-1} and 640 cm^{-1}. We can see that the main component of TiO_2 membranes is anatase phase from Fig.4(c).

The characterization of the sensor was carried out using a sealed gas chamber equipped with valves and mass flow controllers, so that the formaldehyde gas, air and N_2 gas could be introduced separately and mixed. A simple electrical circuit similar to a voltage divider was used to monitor the resistance change of the TiO_2 through a reference resistor R. The sensitivities were calculated under different gas concentrations: $S=R_g/R_a$, where R_a denotes the resistance of the reference resistor before the formaldehyde gas was introduced, and R_g indicates that after the formaldehyde gas was introduced. The sensor shows sensitivities of 15.91 to 7.14 mg/m^3 and 1.54 to 0.04 mg/m^3 formaldehyde concentrations at the operating temperature of diaphragm of 100 °C (Fig.6). The UV LED with 365 nm wavelength, 10 nm bandwidth, size of 1 cm×1 cm and 1 W luminous power was installed on the platform for light activation. However, without UV LED, the sensor has almost no response seen from Fig.5. And so do the sensitivities of 2.17 to 32.94 mg/m^3 and 1.23 to 13.18 mg/m^3 sulfuretted hydrogen concentrations in the same conditions, and the sensitivities of 2.03 to 5 600 mg/m^3 and 1.13 to 4 480 mg/m^3 hydrogen concentrations. When the concentration is below 0.04 mg/m^3, it has no response to formaldehyde; below 16.47 mg/m^3, it has no response to sulfuretted hydrogen; below 4 480 mg/m^3, it has no response to hydrogen. Fig.7 shows the sensor response as a function of formaldehyde concentration. The responses of UV activated TiO_2 to different gases at 100 °C are presented in Fig.8.

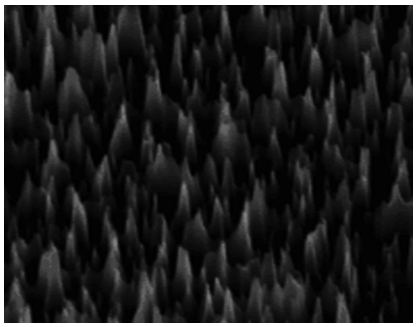


Fig.3 SEM image of microstructure of the black polysilicon

The micro gas sensor shows high sensitivity and fast response to formaldehyde gas in a wide concentration range. Also, the sensitivity to hydrogen and sulfuretted hydrogen is still lower than that to formaldehyde. It may be due to the following reasons: the black polysilicon enhances the gas sensitivity, and the nanoscale TiO_2 membranes deposited by DC reactive magnetron sputtering mentioned above would be more sensitive to formaldehyde.

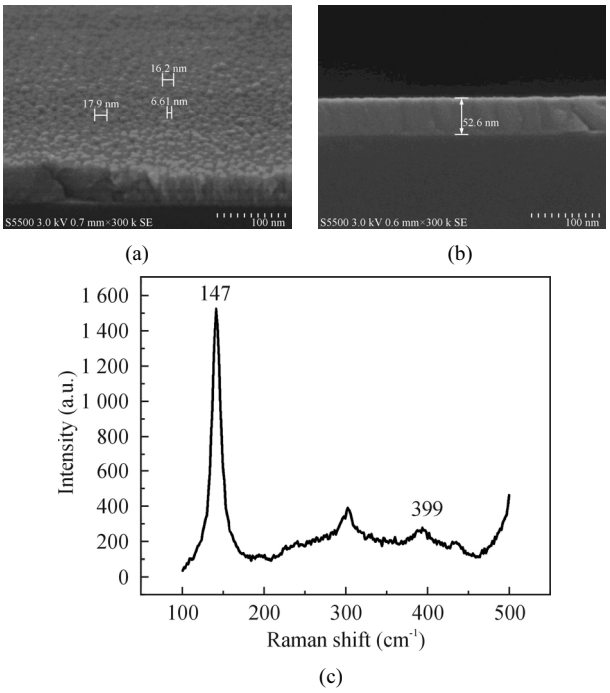


Fig.4 (a) Top view of SEM of the sputtered TiO_2 film; (b) Cross section of SEM of the sputtered TiO_2 film; (c) Raman analysis of TiO_2 film

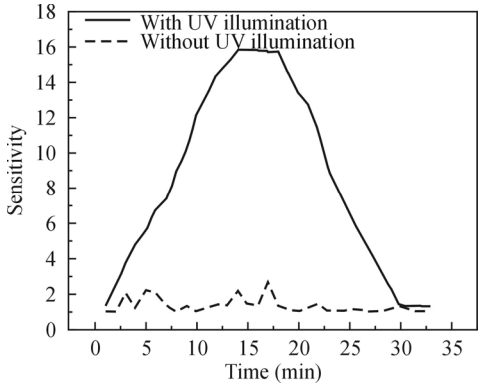


Fig.5 Sensitivity curves of the sensor with and without UV radiation to formaldehyde

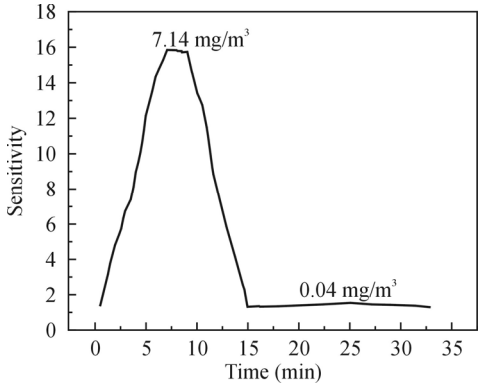


Fig.6 Sensitivity of the sensor to different concentrations of formaldehyde

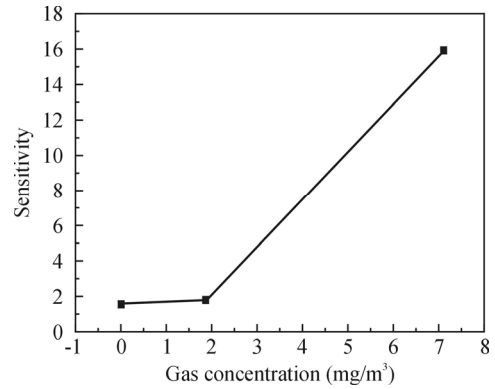


Fig.7 Sensitivity of the sensor as a function of formaldehyde concentration

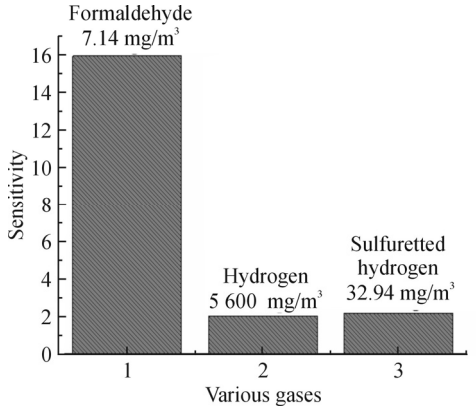


Fig.8 Sensitivities to different gases at about 100 °C under UV radiation

The responses of UV light activated TiO_2 for formaldehyde sensing at 100 °C working temperature are presented in this paper. Using PIII technology to form black polysilicon can make the gas sensor show good sensitivity to formaldehyde, namely, 15.91 to 7.14 mg/m^3 concentration, and the minimum detectable concentration is 0.04 mg/m^3. To other gases, such as sulfuretted hydrogen and hydrogen, the sensitivities are much lower compared with formaldehyde. The innovative approach can enhance gas sensor sensitivity, and the fabrication process is simple, also could be used for mass-production because of the MEMS process compatibility.

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