Micromachined Nanocrystalline Silver Doped Tin Oxide Hydrogen Sulfide Sensor

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ABSTRACT

We report here an ultra high sensitive hydrogen sulfide micromachined gas sensor based on SnO₂-Ag gas sensing material was fabricated on ceramic wafer and quartz wafer. A polymeric sol-gel process has been successfully developed in fabricating thin film SnO₂-Ag nanocomposite, which shows excellent sensing characteristics upon exposure to as low as 1 ppm concentrations of H₂S at low working temperature of 70°C. This sensor shows ultra high sensitivity to H₂S even at extreme (both dry and wet) humidity conditions compared to published results and testing commercial H₂S sensors. SEM was used to investigate surface morphology and crystalline of the film. Selectivity of this gas sensor was studied with comparison with several commercial H₂S sensors; the result shows that this sensor is less sensitive to common interference gases like Cl₂, HCl, SO₂, C₆H₁₄, CH₄, CO, C₃H₈ etc. which may cause false alarm in real applications.

Keywords: MEMS, SMO, Nanocrystalline SnO₂, SWNT Sol Gel

1. INTRODUCTION

Hydrogen Sulfide is a colorless, flammable toxic gas, occurring naturally in crude petroleum, natural gas, volcanic gases, and hot springs with smells like rotten eggs. It can result from bacterial breakdown of organic matter or produced by human and animal wastes. Other sources are industrial activities, such as food processing, coke ovens, craft paper mills, tanneries, and petroleum refineries. H₂S monitoring is very important in industrial areas such as oil and natural gases exploitation plants and coal manufacturing. Electro chemical cell H₂S sensors are mostly widely used commercial sensors, however, it suffers from problems working in extreme environmental conditions (like dry desert) and short life time etc.

Semiconductor metal oxide (SMO) chemical sensors have shown advantages in commercialization prospect and market potential. These advantages include long lifetime, fast response and recovery time, low cost, simple electronic structure and low maintenance [1]. Most research and development of SMO H₂S gas sensors are focused on SnO₂ based and WO₃ based; with few other types reported such s FeNbO₄, BaTiO₃, and TiO₂. Reported SnO₂ based H₂S sensor can be classified as sintered pastes [2], thick [3] and thin film structures using mixed SnO₂-CuO powders, Cu- SnO₂ bi-layers [4], CuO-SnO₂ hetero-contacts [5], chemically fixed CuO on SnO₂ [6-8, 11, 22], Ag₂O- SnO₂, Ag- SnO₂ and SnO₂ -Ag- SnO₂ composite film gate MIS diodes [9, 10, 12]. Other doping material like ZrO to SnO₂ was also reported [13]. WO3 based SMO gas sensor has also been extensively studied as H₂S gas sensor [14-19], Pt and Au are reported to be used as dopant in WO₃ thin film or thick film gas sensor which can detect 1ppm accuracy of H₂S.

The major problems of existing H₂S SMO gas sensor includes cross sensitivity, modest sensitivity, moisture influence, power consumption. In this paper, we report a microfabricated SnO₂-Ag H₂S sensor with advantages of ultrahigh-sensitivity (even in dry conditions), less cross sensitive to interfering gases, low working temperature and power consumption. The sensing material is made of the proper combination of silver as a doping in the nanocrystalline SnO₂, using the sol-gel method. The extreme sensitivity can be contributed to appropriate dispersion of Ag on nanocrystalline SnO₂ grains and uniformity of the nanoporous structure of the films. The

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response of fabricated sensors to staircase concentration of $\text{H}_2\text{S}$, relative humidity change and other interference gases, is discussed in this paper.

2. EXPERIMENTAL

2.1 Gas Sensor Design and Fabrication

Figure 1 shows a schematic diagram of a micro fabricated SMO ceramic substrate sensor, which includes five major parts, namely a substrate, a SMO sensing film, sensor electrodes, a Pt heater and a Pt temperature sensor. The detail of the fabrication process has been reported in [22]. Figure 2 shows the fabricated device fixed on 12 legs package, 1 mil diameter aluminum wires are bonded using an ultrasonic wire bonder.

2.2 SnO$_2$-Ag thin film fabrication by Sol Gel process

Tin isopropoxide ($\text{Sn(O}^{\text{Pr}}\text{)}_4$) was dissolved in anhydrous ethanol. A complexing agent, acetylacetone (AcAc), was added to stabilize the hydrolysis of tin isopropoxide. After complete the mixing using a magnetic stirring, hydrolysis was performed by adding distilled water with an appropriate ratio. A clear and stable sol was formed after continuous stirring. The viscosity of the sol was adjusted with addition of PVA (poly vinyl alcohol). PEG (poly ethyl glycol) was added to improve the plasticity of the coating to prevent cracking during the firing process. AgNO$_3$ was added into the SnO$_2$ sol and followed by a magnetic stirring (for 1 day), while HNO$_3$ was used to stabilize the SnO$_2$ sol. Figure 1 shows SEM picture of SnO$_2$ film doped with Ag.

Fig. 1 Micromachined gas sensor developed

Fig. 2 Fabricated gas sensor

Fig. 3 SEM picture of Ag doped SnO$_2$ film

Nanostructured SnO$_2$ thin film was fabricated by a spin coating and a subsequent sintering process. A ramp spin coating method was used to increase spinning speed gradually up to 1,000 rpm and keep spinning for 30 seconds.
in total. After air-dry the film for 1 min, the coated film was
dried in an oven at 100 degree °C for 30 min. The film
sintering was conducted in a furnace (Thermolyne) with a
heating rate of 2°C/min incensement to 500°C and kept it at
this temperature for 2 hours.

2.3 Gas Sensor Test System
The testing system includes hardware setup and software
program. Hardware setup comprises of five major
components, namely, gas mixing and environmental
condition control, gas testing chamber, data acquisition,
signal output (control), temperature feedback control
circuits [21], and a computer, as are shown Figure 4. The
control program running in PC was written using
LABVIEW. The main function includes data acquisition,
data collection and controlling parameters of the testing
system like Mass Flow Controller setting, feedback
control circuit working temperature setting, etc.

The gas sensitivity was determined by:

\[ \text{Sensitivity} = \left( \frac{R_1 - R_0}{R_0} \right) \times 100 \]

Where \( R_1 \) is resistance values of gas sensing thin film in air,
and \( R_0 \) represents resistance values in gas environment.

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\[ 3. \text{RESULT AND DISCUSSION} \]

Two fabricated SnO₂ sensors doped with Ag are tested in
Hydrogen Sulfide. UCF1 is a sensor made with a quartz
substrate, and UCF2 is small sensor made with a ceramic
substrate. For better understanding our sensor’s
performance, we have included some commercial sensors
include Figaro (Tin oxide) H₂S sensor TGS825, and
Bacharach (SMO) H₂S sensor for comparison.

A staircase concentration test was conducted for H₂S
testing. The procedure was to increase the concentration
from lowest level to highest level. At each level, keep
exposing sensors to H₂S gas for half an hour before
increasing to the next concentration level. UCF1 sensor
is working at 64°C and UCF2 sensor is work at 79°C.
Figure 5 shows the four sensors response in a staircase
concentration experiment.

Figure 5 and Table 1 summarized sensitivities of four gas
sensors at different H₂S concentrations. It is clear that our
fabricated sensor, the UCF1 sensor, has the best
sensitivities over other three sensors. UCF2 and
Bacharach sensors have comparable sensitivities.

Gases like Cl₂, HCl, SO₂, C₆H₁₄, CH₄, CO, C₃H₈, NO₂
etc. are common interference gases, which may cause
false alarm in real applications. In this study, we
conducted test for the following concentrations of

\[ \text{Fig. 4 Testing System Setup} \]

\[ \text{Fig. 5 Step Concentration H₂S Test Result} \]

\[ \text{Fig. 6 Selectivity Test Result} \]
interference gases: Cl₂ (10ppm), HCl (10ppm), NO₂ (5ppm), HCN (10ppm), SO₂ (9ppm), C₆H₁₄ (0.3%), CH₄ (2.2%), CO (50ppm), C₆H₁₄ (0.44%). Figure 6 shows the interference gas test result, it is obvious that our fabricated sensors are less sensitive to common interference gases compared to Figaro and Bacharach sensors. For NO₂ case, all sensors have large response. However, since the NO₂ is oxidizing gas, exposure to them will make the SMO sensor’s resistance increasing instead of decreasing. Therefore, the risk of causing false alarm is small.

4. CONCLUSION

We have developed microfabricated Ag-SnO₂ thin film gas sensor with ultra high sensitivity and selectivity to H₂S detection. Ag doped nanocrystalline SnO₂ gas sensing material was successfully prepared with sol gel processes. The Ag-SnO₂ films showed better sensitivity compared to pure SnO₂ due to proper dispersion of Ag₂O particles between nanocrystalline SnO₂ grains and formation of p-n hetero junctions. The H₂S measurements were carried out for staircase concentration at an operating temperature as low as 64 C. A high sensitivity was obtained for 1ppm H₂S. The selectivity of the sensors was studied for various inference gases; the result shows that our fabricated sensors are less sensitive to common interference gases compared to some commercial H₂S sensors like Figaro and Bacharach sensors.

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Table 1: Sensitivity Summary of Step Concentration Test

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