Sol-Gel Prepared Single Wall Carbon Nanotube SnO_2 Thin Film for Micromachined Gas Sensor

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ABSTRACT

We report here a novel micromachined single wall carbon nanotube (SWNT)/tin dioxide (SnO_2) nano film gas sensor. A polymeric sol-gel process in combination with purified SWNT has been successfully developed in fabricating SWNT/SnO_2 thin film nanocomposite sensor on an alumina substrate. The test of the novel nanocomposite gas sensors has been conducted for hydrogen detection, in comparison with sol gel derived SnO_2 thin film. The test results show that SWNT has greatly improved the nano-SnO_2 thin film's gas sensing property, in terms of lower working temperature, greater sensitivity (a factor of 3), faster response time and recovery time, and less drift of resistance. The improved capabilities are credited to the large surface to volume ratio of gas sensing thin film with nano passes created by SWNT, and the distance between adjacent passages being less than electron depletion layer thickness is defined by SWNT. The fabrication process is compatible with IC industry thus it is cost effective for batch production.

***Keywords*:** MEMS, SMO, Nanocrystalline SnO_2, SWNT Sol Gel

1. INTRODUCTION

Semiconductor Metal Oxide (SMO) gas sensors have been studied for decades owning to their advantages of more robust, less sensitive to moisture and temperature, simple interface electronics, faster response time and recovery time [1]. SMO gas sensors based on pellets or thick film technology are normally not chosen for the fabrication of intelligent Microsystems. This is not only due to processing incompatibility but also due to the high power consumption. Therefore, SMO thin film gas sensor has been regarded as the next generation gas sensing elements. In recent years, nanotechnology has emerged for developing novel gas sensing materials with unusual properties. Nanotechnology has proven very promising in SMO gas-sensing materials. Since SMO's gas detection principle is based on variations of the depletion layer at the grain boundaries, when either reducing or oxidation gases are present. As the results, the adsorbed gas leads to a variation in the height of the energy barriers for free charge carriers (e.g. electrons in SnO_2) [2]. When particle size decreases, the ratio of the depleted volume to the whole bulk grain volume increase greatly (related to the surface to volume ratio which is reverse proportional to the particle size). It is recognized that SnO2 semiconductor thin film can have maximum gas sensitivity only if the nanocrystallite size within the film is comparable with its space-charge layer thickness (3nm for SnO_2, [3]). Currently most SnO2 films are fabricated with physical vapor deposition and sol gel process. The grain size is normally in a range of 10nm to 100nm, which is larger than the depletion thickness (3nm).

Carbon nanotubes (CNTs) are hollow nano pipes that could be used to provide nano passes in sensing materials. The CNTs are also proven gas sensors such as oxygen [4] and carbon dioxide [4], nitrogen oxide (NO_2) methane [5], and ammonia (NH_3)[6]. Single walled carbon nanotubes (SWNT) have limitations in detecting some gases such as CO [6], while SnO_2 does have good response to a wide range of chemical gases.

The objective of this research article is to take advantage of both SnO_2 and SWNT and to improve SnO_2 gas sensing property in terms of sensitivity, response time and recovery time by using SWNT reinforcement. The function of SWNT can be summarized into two-fold. The first one is

using SWNT to achieve permanent nano passes for gas sensing after sintering SnO_2. The second one is using SWNT to define the distance between gas accessing boundaries to be less than two time of depletion zone of SnO2 (6nm).

MEMS (Micro-Electro-Mechanical-System) has been relative more mature than nano technology. By combing nanotechnologis with MEMS techniques, novel gas sensor has been developed and it is described in this article. This approach provides low cost minimized device that lower power consumption and compatible to IC fabrication will be realized.

2. EXPERIMENTAL

2.1 Gas Sensor Fabrication

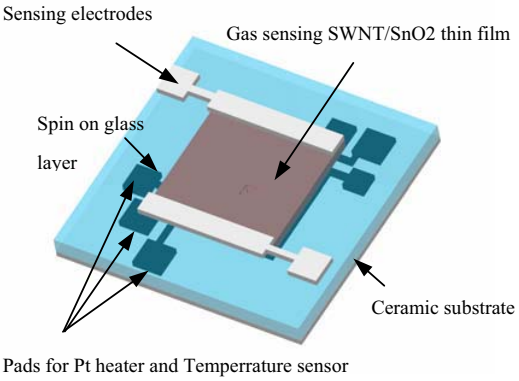

Fig. 1 Micromachined gas sensor developed

The MEMS based gas sensor cell is sketched in Figure 1 and the microfabrication process is shown in Figure 2. Aluminum wafer was used as substrate for better thermal and electrical isolation. Thin film Pt is used as micro heater and temperature sensor and it was fabricated by thermal deposition and lift off process. High dielectric spin-on glass was spin coated on as the electric isolation layer. SnO2/SWNT gas sensing thin film was fabricated by spin coating prepared Sol. The sensing electrode was deposited on top by thermal evaporation and patterned by liftoff after sintering the SnO_2 film.

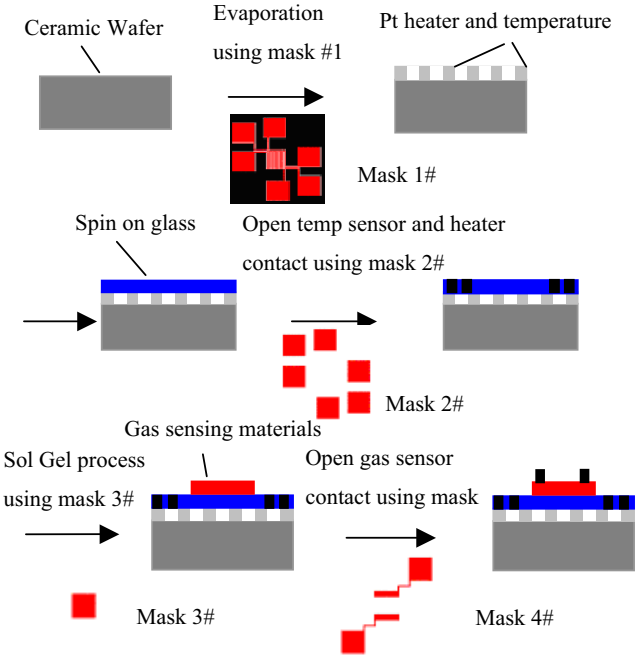

Fig. 2 Fabrication Process of gas sensor

2.2 Preparation of Sol

Porous nanocrystalline tin oxide layer was developed by polymeric sol gel technique. A precursor of tin isopropoxide ($Sn(O^iPr)_4$, 10%, Alfa Aesar) 25ml was firstly dissolved in 50ml isopropyl alcohol followed by magnetic stirring for half an hour. Then a complexing agent, acetylacetone (AcAc) 3ml was added to stabilize the hydrolysis of tin isopropoxide.

2.3 SnO_2 thin film by Sol Gel process

Nanostructured SnO_2 film was fabricated by sol gel spin coating followed by sintering. During spin coating, the rotating speed was gradually increased to speed up to 3,000rpm for 30 seconds. Then the gel film was dried in air for 10 min. The process was repeated for 3 times until desired thickness was achieved. After spin coating, the gel film was dried in an oven at 100°C for 30 min. Finally, sintering was done in a furnace with a heating rate (2°C/min) to 500°C and kept for 2 hours). Fig. 3 shows an SEM micrograph of nano SnO_2 film (grain size is about 15nm).

Acquired SWNT was mixed into a SnO_2 sol, after a specific purification process developed. After 24 hours of magnetic stirring and another 10 min of ultrasonic cell disrupting, the

light dark transparent sol solution containing SWNT suspension is obtained. The SWNT's diameter is approximately 1.4 nm. The viscosity of the sol was adjusted with addition of PVA (poly vinyl alcohol). After sintering at 500°C within an argon environment for 2 hours, nano-sized SnO_2 containing uniformly distributed SWNT is indicated in Figure 4, in compared to pure SnO_2 particles (Figure 3).

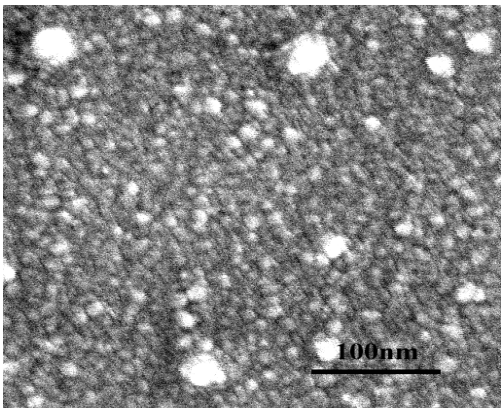

Fig.3 SnO_2 grains (15nm) after sol gel process

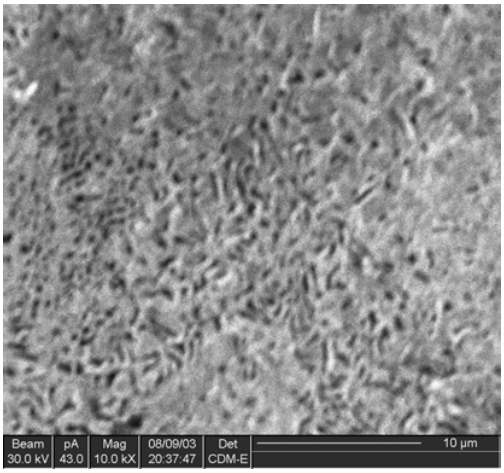

Fig. 4 SWNT wrapped by nano sized Tin dioxide

2.4 Gas Sensor Test System

The testing system includes H_2, N_2 and pure air gas cylinders with regulators (Airgas), 2cc/min mass flow controller (Omega), flow meter, gas chamber oscilloscope (TDS 224) and NI data acquisition system. The gas sensitivity was determined by:

$$\text{Sensitivity} = (R_1\text{-}R_0)/R_0 \times 100$$

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

3. RESULT AND DISCUSSION

Both pure nano SnO_2 and SWNT enhanced nano SnO_2 sensors were tested in 1500ppm hydrogen under different temperatures for comparison. Typical tested results are presented in Figure 5 and the comparison is presented in Table 1. It is obvious that SWNT/SnO_2 composite sensor has much better gas-sensing properties than the pure SnO_2 sensor. The sensitivity is 3 times higher (Table 1) at various temperatures tested. It has a good sensing at low temperatures (150°C) at which the pure SnO_2 doesn't. The undoped SWNT/SnO_2 sensor has much better sensitivity than doped with catalysts [7].

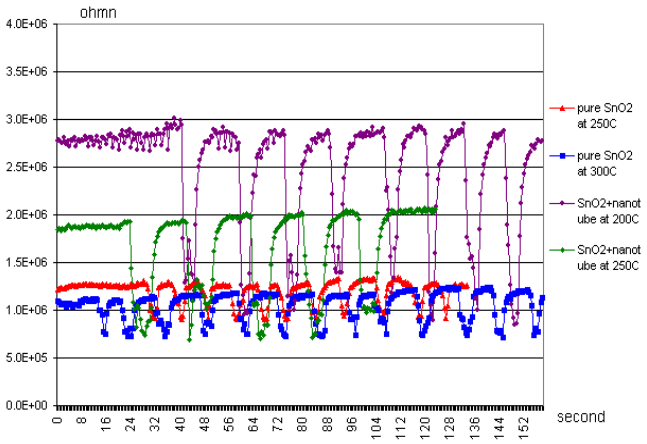

Fig. 5 Comparison of various test results in 1500ppm

Table 1: Comparison of Pure SnO_2 sensor and SWNT/SnO2 sensor at different working temperature

	Sensitivity	Response time	Recovery time
Pure SnO2 at 150°C	N/A	N/A	N/A
SnO2/SWNT at 150°C	~50%	5~7s	15~18s
Pure SnO2 at 200°C	~39%	5~7s	25~30s
SnO2/SWNT at 200°C	~115%	3~5s	3~5s
Pure SnO2 at 250°C	~40%	3~5s	6~8s
SnO2/SWNT at 250°C	~147%	2~3s	4~5s
Pure SnO2 at 300°C	~56%	3~5s	5~7s

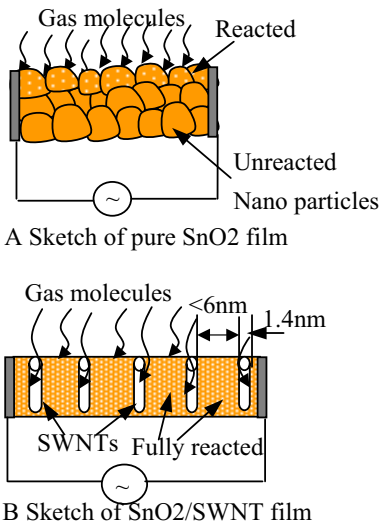

Fig. 6 Sketch of gas sensing mechanism between pure SnO2 film and SnO2/SWNT film

The enhanced sensitivity of nano SnO_2/SWNT thin film attributes to two aspects as sketched in Figure 6. First, SWNT provide permanent nano passes for gas sensing after SnO_2 sintering. As a result, the surface to volume ratio increases largely, which leads to better sensitivity. Secondly, SWNT with 1.4 nm diameters was used to define the distance between SnO_2 crystalline grains and thus confine gas-accessing boundaries to be less than 6nm. According to the model brought up by Xu et al. [8], depending on the nanocrystalline size (D) relative to its space charge layer thickness (L), the transducer function is operated by a mechanism of grain-boundary control (D>>2L), neck control (D>2L) or grain control (D≤2L), respectively. The gas sensitivity of nanocrystalline SnO_2 thin film is enhanced only when the film resistance is controlled by the latter two mechanisms, especially by the grain control mechanism. For the SnO_2 thin film, the space-charge layer thickness has been calculated to be ~3 nm at 250 ^oC [8]. As a result, the sensitivity increase steeply as *D* decreases to be comparable with or less than 2*L* (≅ 6 nm).

4. CONCLUSION

MEMS based sensor with nanocrystalline SnO_2/SWNT sensing films was developed using polymeric sol-gel process in combination with purified SWNT. Compared to pure SnO_2 type, this sensor produce improved sensitivity (by a factor of 3), faster response time and recovery time to 1500ppm hydrogen at even relatively low working temperature. Since this gas sensor is fabricated using micro fabrication process, the power consumption is limited to low level, MEMS based device also make low cost per device possible.

5. ACKNOWLEDGEMENTS

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