

Development of Micromachined Nanocrystalline Mesoporous SnO₂ Gas

Sensor for Electronic Nose

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ABSTRACT

MEMS based sol gel synthesized mesoporous nanocrystalline SnO₂ gas sensor has been developed. The SnO₂ nano film is fabricated with the combination of polymeric sol gel chemistry with block copolymers used as structure directing agents. The novel hydrogen sensor has a fast response time (1s) and quick recovery time (3s), as well as good sensitivity (up to 90), comparing to other hydrogen sensors developed. The working temperature of the new sensor can be reduced as low as 100 °C. The low working temperature poses advantages such as lower power consumption; lower thermal induced signal shift as well as safe detection in certain environments where temperature is strictly limited. The developed sensor cell will be used to develop a high sensitivity and high selectivity electronic nose for harmful gas detection by combining different catalysts doped SnO₂ gas sensor array with fuzzy neural network.

KEYWORDS

MEMS, SMO, Nanocrystalline, Triblock Copolymer, Electronic Nose

INTRODUCTION

To date, no gas sensor exists that is 100% selective to a single chemical gas¹, therefore, a gas sensor array able to detect different interested gases have been a major focus of research on gas sensors for years. Electronic Nose (Sensor Array) is widely used in many fields like environmental monitoring (HVAC system air quality control, e.g.), safety and anti terrorism (explosive (bomb) gas and toxic gas detection in public area like airport, shopping center etc.), odors detection in industries (food, drinks, fragrance, chemical, etc.). Analytical systems such as Fourier Transform Infrared (FTIR), Gas Chromatographs and Mass Spectrometers are good detection tools but have problems as: requirement of skilled and knowledgeable operators, very expensive of equipment and high maintenance cost, slow response time, and large in size that is not good for deployment. A desired portable gas detection system should be rugged and corrosion resistant, capable of being installed in hazardous areas, durable for long term, operationally stable, simple in maintenance, enable for a minimally skilled person to operate and cost effective, etc.

In the past 5 decades, semiconductor metal oxide (SMO)

gas sensors have emerged as efficient gas detection tools. Compared to other gas sensing techniques like conductive polymer (CP), Oscillating methods such as QMB and BAW/SAW, Electrochemical Cell and Fiber Optical, SMO gas sensors have advantages of more robust (up to 10 year life time), less sensitive to moisture and temperature, simple interface electronics, have faster response time and recovery time². SMO gas sensor can detect the maximum range of gases such as SnO₂, while this means selectivity may not be good at the same time. Sufficient selectivity can only be achieved if several sensors are put together to form an array. In this case, a lack of selectivity but a wide range of sensitivity (overlapping between different sensors) can be turned into an advantage³. MEMS based SMO gas sensor is fabricated using IC compatible process, which means low cost due to batch microfabrication. Therefore, SMO gas sensor is the best choice for Electronic Nose.

The gas detection principle of semiconductor type gas sensor is based on variations of the depletion layer at the grain boundaries in presence of reducing or oxidation gases which lead to variation in the height of the energy barriers for free charge carriers (e.g. electrons in SnO₂). When particle size decreases, the surface to volume ratio increase largely

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(reverse proportional to the particle size). Thus nano sized particles with high porosity produced by sol gel offer excellent opportunities for gas detection. Up to date, block copolymers have been used to fabricate particles, fibers and thin films of various mesoporous oxide (SiO_2 and Al_2O_3) with various pore sizes (2 to 30nm) ^{4,5}. Since block copolymer is a convenient group of structure-directing agents for a wide range of oxides, this method can be extended to tin oxide.

In this research, gas sensor cell with mesoporous Tin Oxide thin film has been fabricated and tested. The developed sensor cell will be used to develop a high sensitivity and high selectivity electronic nose for harmful gas detection by combining different catalysts doped SnO_2 gas sensor array with fuzzy neural network.

EXPERIMENTAL

Gas Sensor Fabrication

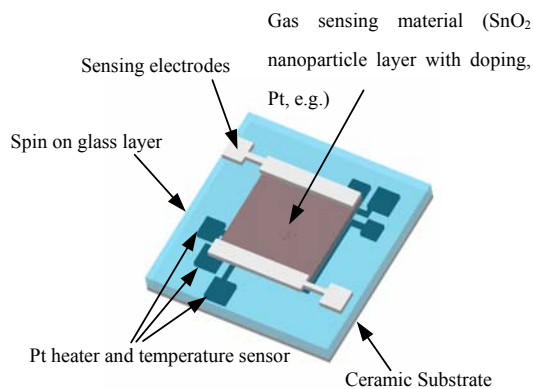


Figure 1 Single proposed gas sensor cell

The MEMS based gas sensor cell is sketched in Figure 1. Alumina wafer was used as substrate for better thermal and electrical isolation purpose. Pt micro heater and temperature sensor was fabricated by thermal deposition and a lift off process. High dielectric spin-on glass was spin coated on as the electric isolation layer. Gas sensing thin film was fabricated by spin coating prepared sol. The sensing electrode was deposited by thermal evaporation and patterned by liftoff after sintering the SnO_2 film.

Preparation of Sol

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

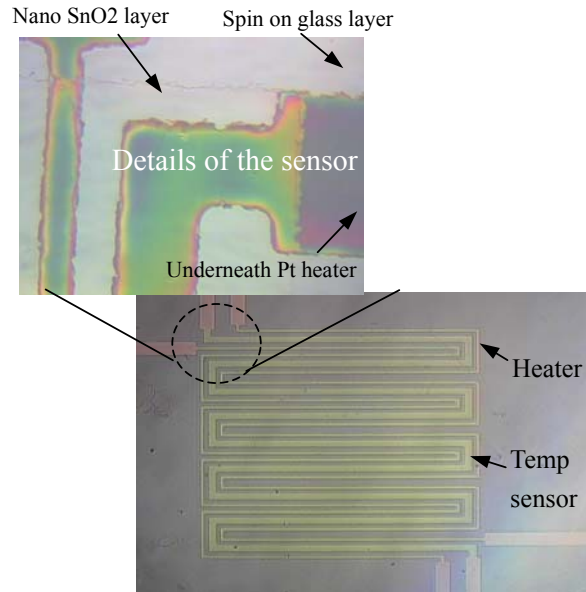


Figure 2. 500X Microscopic Picture of fabricated device

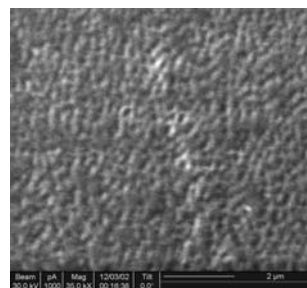


Figure 3. Porous structure of SnO_2 surface with nano-size particles under 35k X

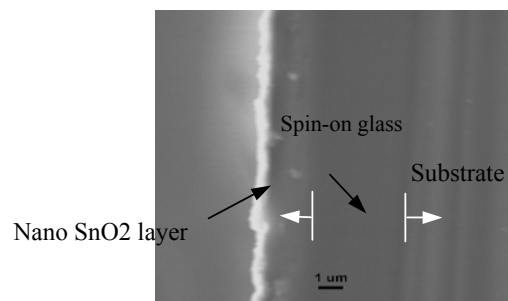


Figure 4. SEM picture show thickness of nano particle and the spin-on glass layer

After mixing completely using magnetic stirring for 2 hours, 10wt% triblock copolymer Pluronic F127 (PEO-PPO-PEO) was dissolved into the solution followed by 2 day completely mixing. The viscosity of the sol was adjusted with addition of PVA (poly vinyl alcohol).

SnO₂ thin film by Sol Gel process

Nanostructured SnO₂ film was fabricated by spin coating and sintering. Spin coating the sol at gradually increasing rotating speed up to 5,000rpm for 3 min. After air-dry the film for 5 min, another spin coating and air-drying applied and repeated for three times. Dry gel was baked in oven at 100 degree C for 30 min. Then it was sintered in a furnace (2° C/min incensement to 500 ° C and keep for 2 hours). Fig. 3 shows the mesoporous structures of nano SnO₂ particles. Fig. 4 shows the cross section of films after fabrication.

Dopants and Catalysts

When preparing SnO₂ sol, dopant of silver nitride (AgNO₃) can be easily added to achieve the atomic mixing. Prepared SnO₂ sol is equally divided into two. AgNO₃ was added into one of these two sols followed by a magnetic stirring process for 1 day. HNO₃ was used to stabilize the sol.

To achieve higher sensitivity to some reducing gases, catalyst metal of Pt was introduced by sputtering process, after SnO₂ thin film was spin coating and annealed. Pt is sputtered onto surface of SnO₂ thin film followed by thermal diffusion. A fabricated sensor cell prototype is indicated in Figure 5.

Test

The testing system includes H₂, N₂ etc. gas cylinder with regulators (Airgas), a 2cc/min mass flow controller (Omega), flow meter, gas chamber oscilloscope (224) and National Instrument (NI) data acquisition system. The gas sensitivity was determined by:

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

Where R₁ is resistance values of gas sensing thin film in air, and R₀ represents resistance values in a environment.

Fabricated gas sensor cell with SnO₂+Pt thin film was tested in a gas consists of 100ppm hydrogen. The raw test result is shown in Figure 6. Another gas sensor cell with SnO₂+Ag+Pt thin film was also tested in 100-ppm hydrogen and the raw result is shown in Figure 7. An undoped pure SnO₂ thin film sensor was fabricated and tested for sensitivity study to hydrocarbons. The tested results on acetone and ethanol are shown in Figure 8.

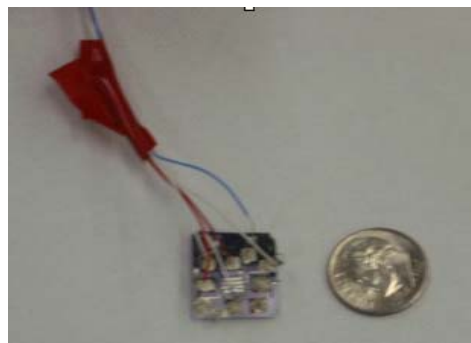


Figure 5 Fabricated silicon based gas sensor cell

RESULT AND DISCUSSION

For SnO₂+Pt thin film gas sensor, good sensitivity can be found at 100°C even though better results achieved at 200°C and 300°C. This sensor has a fast response time (1s) and quick recovery time (3s) to hydrogen, as well as good sensitivity (up to 90 at 300°C).

For SnO₂+Pt+Ag thin film gas sensor, we can observe less drift, better sensitivity and faster response time, which proved that doped Ag improves the sensing ability of SnO₂ thin film to Hydrogen.

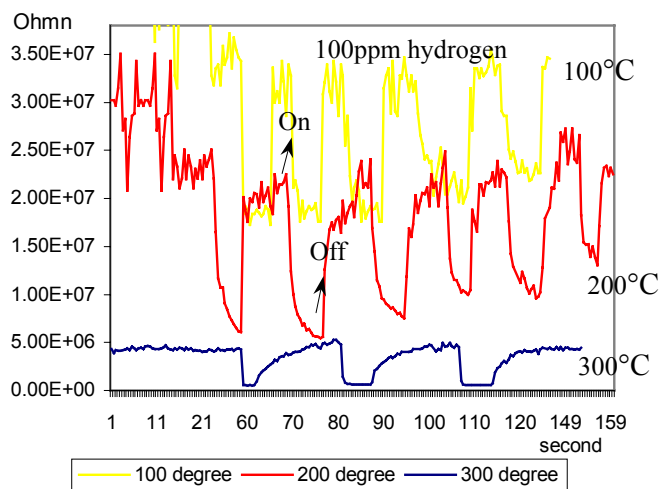


Figure 6 Response of SnO₂+Sputtered Pt to 100ppm H₂

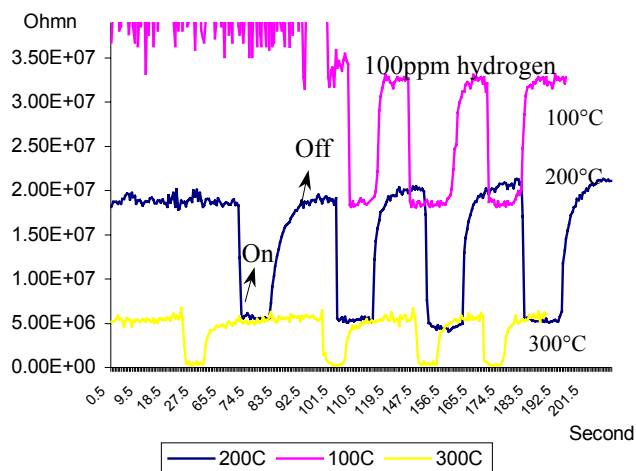


Figure 7 Response of SnO₂+5% Ag+ Sputtered Pt to 100 ppm H₂

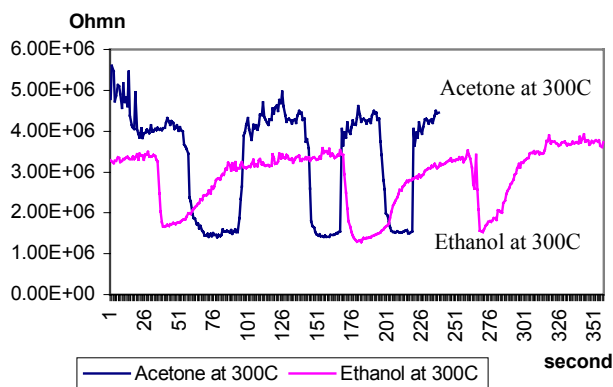


Figure 8 Response of pure SnO₂ thin film to Acetone and Ethanol

The enhanced sensitivity of nanocrystalline SnO₂ thin film attributes to two aspects. First, when particle size decreases, the surface to volume ratio increases largely (reverse proportional to the particle size), which leads to better sensitivity.

Secondly, the porous topology of gas sensing thin film has great impact on gas sensing behavior. In this investigation, block copolymer as a convenient group of structure-directing agents, has been applied during sol preparation. The mesoporous tin oxide thin film fabricated using this sol gel process has large amount of film porosity, which also contribute to the enhanced sensitivity. N. S. Baik et al¹¹ contribute this phenomenon to an enhanced Knudsen diffusion coefficient (D_k). For

straight round pores within the film, D_k is given by,

$$D_k = 9700 \times r \times (T/M)^{1/2}$$

Where, r is the pore radius, T the absolute temperature (K), and M the molecular weight of the gas. For a given film thickness, larger pore radius increases D_k , and hence, would favor the improved gas concentration profile.

The thickness of nanocrystalline SnO₂ thin film is also important factor that greatly affect gas sensitivity. Unlike TiO₂, which is bulk conductance effects semiconductor, SnO₂ belongs to the surface conductance effects semiconductor. The interaction between a SnO₂ surface and H₂ (with reducing properties) can be explained in terms of reaction of hydrogen molecules with the preadsorbed oxygen (Figure 9).

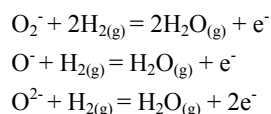
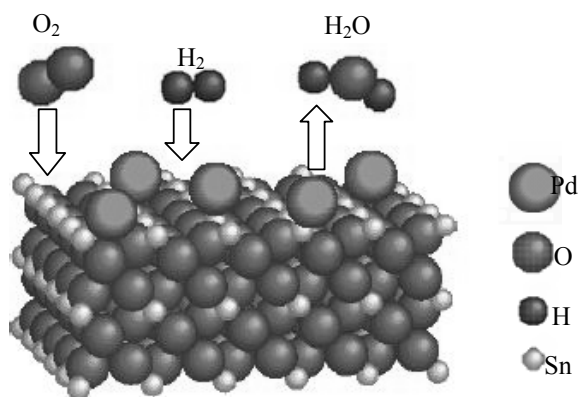


Figure 9 Illustration of principle of SnO₂ sensor in detection of H₂

S. Shukla et al.¹³ proposed that gas sensitivity of nanocrystalline SnO₂ thin film increases which increases with decreasing the film thickness. However, below a critical film thickness of ~110 nm, the gas sensitivity decreases with further decrease in the film thickness. Very compact films exhibit lower surface areas and reduced Knudsen diffusion coefficient. As a result, they offer reduced number of active sites for the oxidation reactions with the reducing gases, and hence, would reduce the gas sensitivity with decreasing film thickness below this critical

thickness range. In this investigation, the nanocrystalline SnO₂ film thickness of 100~150 nm was obtained via sol-gel spinning coating process under strictly controlled processing conditions.

For pure SnO₂ thin film, the experiment results shown in Figure 8 illustrate that its sensitivity to different hydrocarbon is good, this broad range sensibility to different gases cause cross sensitivity (restrictive selectivity) which is preferable for Electronic Nose application. By adding different dopants and catalyst, certain gas sensor cell will have better response to certain interested gas while common response to other existing gases, these cross sensitivities can be analyzed by Artificial Neural Network as long as it is trained (calibrate) before usage.

In future work, the sensor cell developed will be put into gas sensor array (different dopants and catalysts for specific gas) as is shown in Figure 10. TSK fuzzy neural network will be applied for data processing in the electronic nose system.

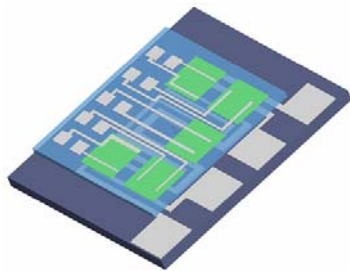


Figure 10 Sketch of the sensor array (electronic nose system)

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