Particle Size and Film Thinness of TiO_2 Sensor Prepared by Flame Synthesis

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Abstract. Nanostructured semiconducting metal oxide (SMO) gas sensor can be fabricated with flame synthesis by combusting a premixed fuel-oxidizer mixture doped with a selected metal precursor in the stagnation flow configuration. Particle size and film thickness of the SMO sensor are the most significant parameters for the sensing performance. Thus, they should be well predicted and properly controlled. In this study, some experiments on the particle size and film thickness were conducted. It was found that the particle size was mainly depended on the concentration of precursor. Results shojwed that the growth rate increase firstly then decrease with time. A TiO_2 gas sensor was then prepared by flame synthesis directly with desired particle size and film thickness at a given precursor concentration. After proper post-processing, the CO sensing properties of the TiO_2 sensor were tested under different testing temperatures. The sensor showed excellent performance in sensitivity and response time, and the optimal testing temperature was around 500^{o}C.

Introduction

Gas sensor is a kind of device that can convert gas composition to electrical signal or other measurable signal. [1]The application of gas sensor is quite widespread, both for home and industry. On one hand, the detection of toxic gas indoor is crucial for the people healthy. Gas sensor is needed to monitor the air quality indoor, as it has become an essential part of modern house. [2]On the other hand, gas sensor is of vital importance for industrial application. For the steel, energy and metallurgy industry, emission monitoring for NO_x, SO_x, CO mainly depend on high-performance gas sensor.

Flame synthesis[3, 4] has been introduced to the preparation of nano-SMO gas sensor[5] for decade. The preparation process can be classified as indirect film formation method and direct film formation method. Up to now, most of the researchers focus on the indirect film formation method, which means separating the process of particle synthesis and film formation. C. Liewhiran & S. Phanichphant (2008)[6] prepared Pd/ZnO gas sensor for ethanol alcohol detection by doctor blading method. Results show that the range of measurement can reach 20 ppm ~ 400 ppm at the temperature of 400^{o}C. F. PADINGER et al (2000)[7] also applied doctor blading method to prepare light-sensitive device. Doctor blading is a common method for indirect film formation method, which need complicated pre-processing and post-processing. Direct film formation method is more competitive as it can combine process of particle synthesis and film formation together. Zili Zhan et al. (2010)[8] prepared the SnO_2 film for gas sensor by flame synthesis directly, and studied the influence of synthesis condition. Erik Tolmachoff et al. (2011)[9] prepared TiO_2 sensors by direct film formation and indirect film formation method simultaneously, comparing the sensing properties of the two sensor. Results show that sensor prepared by direct film formation method is more superior in sensitivity and stability for CO detection.

In all, direct film formation by flame synthesis is a promising way for the preparation of nano-SMO gas sensor. Current research mainly focus on the indirect film formation method, a systematic study for the direct film formation method by flame synthesis to prepare nano-SMO sensor is necessary. This paper is to develop a test rig to prepare SMO gas sensor by flame synthesis directly, and preliminary study for the sensing properties of the sensor will be done.

Experimental

Substrate of Sensor

The substrate of sensor is designed as Figure 1, Au film is pre-coated on the board with a thickness of 5μm by sputtering, arranging in interdigitated structure. The width of Au line is 250μm, and 250μm for the gap between the positive and negative electrodes. The overall size of the substrate is 30mm×15mm×0.76mm.

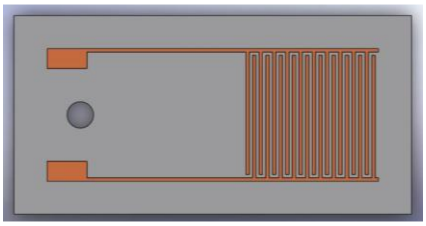

Fig.1 Schematic of sensor substrate

Flame Synthesis Test Rig

A stagnation flame synthesis test rig is developed to prepared nanostructured SMO film, which is the critical part of gas sensor. There are four main parts, including the gas system, precursor injection system, combustion/deposition system and ventilating system, as showed in Figure 2. The gas system provide premixed CH_4, N_2 and O_2 as fuel, with an equivalence ratio of $\varphi = 0.68$. The liquid precursor, Titanium isopropoxide (TTIP), is injected into the premixed gas by syringe. In order to ensure the fully vaporization of the precursor, the premixed gas must be preheated to 150°C by heating tapes. The premixed gas, combining with precursor, is burned at the nozzle, stabilized by a stagnation surface of copper plate cooled by circulating water. The huge temperature gradient between the flame sheet and copper plate provides thermophoresis force, which can help the particles deposited on the disk directly. The substrate of sensor is fixed on the copper plate, holding the particles from the gas phase. The whole test rig must be well ventilated, since most of the particles in the flame will diffuse to the atmosphere.

The porosity of the initial SMO film prepared by flame synthesis is relatively large, almost 90%, some post-processing is necessary for gas sensing. Firstly, the initial film must be densified by the solution of ethyl cellulose in ethanol, in order to reduce the distance between particles. Secondly, the densified film should be sintered in muffle furnace at a temperature of 600°C for 4h, ensuring fully growth of the grain boundary between praticles. Then, a SMO film with gas sensing properties is done.

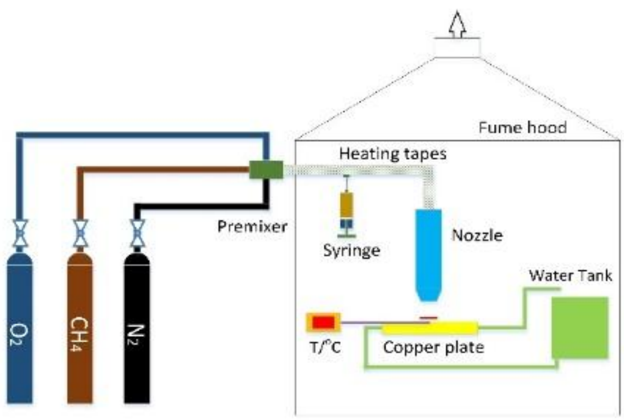

Fig.2 Schematic of Flame Synthesis Test Rig

Gas Sensing Properties Testing Rig

A test rig is developed to evaluate the sensing properties of gas sensor prepared by stagnation flame synthesis directly, which is the main objective of the paper, as showed in Figure 3. There are three main parts, including gas system, high-temperature testing platform and resistance measurement and acquisition system. The target gas is prepared by mixing dry Air and CO by different ratio, and the flowrate is controlled by mass flowmeter. The target gas, with certain CO concentration, is led to the sensor surface. High temperature is necessary for the application of gas sensor, which is provided by high-temperature testing platform. The platform is heated by ceramic heating chip, which is controlled by temperature controller. The resistance of sensor is measured by bleeder circuit with a standard resistance under bias voltage. The voltage on the standard resistance can be measured by digital multi-meter (Agilent 34401A), and data is collected by computer on-line. The resistance of the sensor can be determined according to voltage on the standard resistance. Therefore, the resistance of gas sensor in different atmosphere can be measured, which is the foundation for the evaluation for the sensing properties.

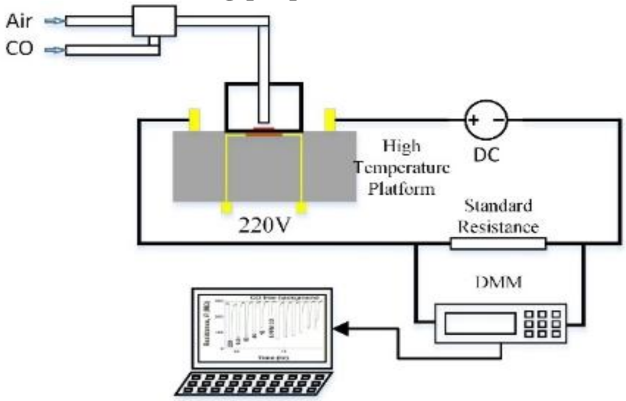

Fig.3 Schematic of Gas Sensing Properties Testing Rig

Results

Characterization of Particles

In order to study the influence of the concentration of precursor, seven concentration values are selected, namely 500ppm, 800ppm, 900ppm, 1000ppm, 1100ppm, 1300ppm and 2000ppm, with an error range of 1%. CH_4, N_2 and O_2 are premixed with an equivalence ratio of φ = 0.68. Titanium isopropoxide (TTIP), as the precursor, is injected into the premixed gas, which is preheated to 150^{o}C to ensure the fully vaporization of the precursor. The stagnation surface is cooled by circulating water at a temperature of 200^{o}C. The distance between the outlet of the nozzle and the stagnation surface is fixed at 14mm. For every precursor concentration, the deposition time is set as 30s. The particles will be characterized by TEM and BET simultaneously.

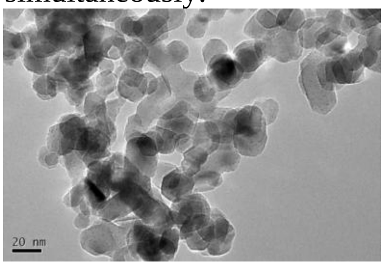

Fig.4 TEM Image of TiO_2 Particle (TTIP, 2000 ppm)

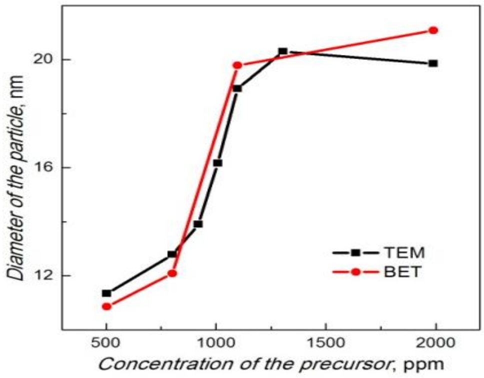

Fig.5 Curves of Particle Diameter to Precursor Concentration by TEM and BET

Figure 4 is the TEM image of particles prepared with the TTIP concentration of 2000ppm, as we can see that the particles are relatively uniform. According to the TEM images, diameter of particles with different precursor concentration can be determined. Meanwhile, the specific area of particles, which can also determine the particle diameter, is measured by BET. Figure 5 is the relation curves of particle diameter to precursor concentration by TEM and BET. Results show that higher concentration of precursor is beneficial to produce larger particles. The slope of the curve is first increase then decrease. Especially, diameter of particles increase almost linearly with the concentration of precursor at the range of 800ppm to 1000ppm. Excessing 1300ppm, the diameter will not increase with the concentration of precursor, which means there is a saturation concentration of precursor for the synthesis of particles. The characterization of particles is an important reference for controlling the properties of gas sensor.

Characterization of Film

The controllability for the film properties is an important index for the preparation method. Thickness of film is one of the most fundamental parameters for the nano-SMO film, which can affect the sensor properties. Therefore, well control of the thickness of SMO film is quite important for the properties of gas sensor. This paper studies the relation between the concentration of precursor and the thickness of film. The concentration of precursor is fixed at 1000ppm, and fourteen deposition times were selected ranging from 20s ~ 500s. The thickness of film is measured by a Three-dimensional surface of white light interference profile meter.

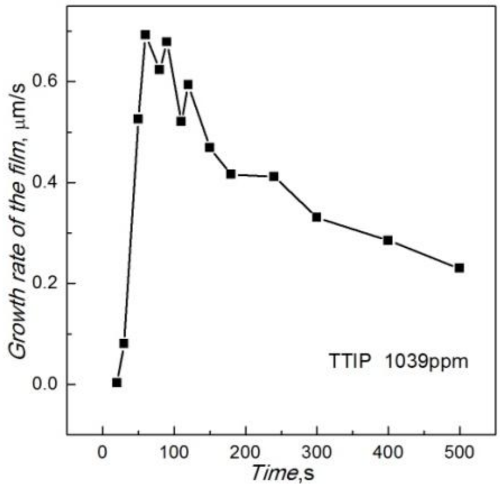

Fig.6 Curve of the Growth Rate of Film to the Deposition Time

As showed in Figure 6, the growth rate of film is increasing firstly and then decreasing to the deposition time with the precursor concentration of 1000ppm. The growth rate is relatively stable at the range of 60s ~ 120s, with a maximum value of 6.5μm/s. It is easy to understand that the growth rate is low during the prior period, since the clean and smooth surface is not benefit for the capture of particles. When there is a layer of particles deposited on the surface for a period, the rough surface will promote the capture of particles, which leads to the increase of the film growth. However, after long period of deposition, the thick film will cause great temperature gradient. Then the temperature gradient between the flame sheet and the upper layer of film will decrease, reducing the thermophoresis force, which will cause the decrease of the film growth rate. Further work is to be done to determine the influence of precursor concentration to the film growth rate.

Sensing Properties Testing of Gas Sensor

The preparation condition is listed as follow: CH_4, N_2 and O_2 are premixed with an equivalence ratio of φ = 0.68, being preheated to 150°C to ensure fully vaporization of the precursor. TTIP, as the precursor, is injected into the premixed gas with a concentration of 500ppm. The distance between the outlet of nozzle and the stagnation surface is 14mm. Temperature of the stagnation surface is fixed at 200°C. The deposition time is 40s. The diameter of TiO_2 particles is estimated to 10nm according to the previous results. The initial TiO_2 film is densified by ethyl cellulose solution, and then sintered in muffle furnace at a temperature of 600°C for 4h. Then, a TiO_2 gas sensor for CO detection is done.

The sensing properties of the sensor for CO detection has been done by the test rig. The target gas is prepared by mixing CO and dry air (balancing gas) with different ratio, getting three CO concentration of 150ppm, 300ppm and 600ppm. Flowrate of the target gas is controlled by PLC, mixed gas and dry air are piped to the surface of TiO_2 sensor for 3min respectively. The bias voltage applied on the sensor is 3V, and the testing temperature is 450°C, 500°C and 550°C.

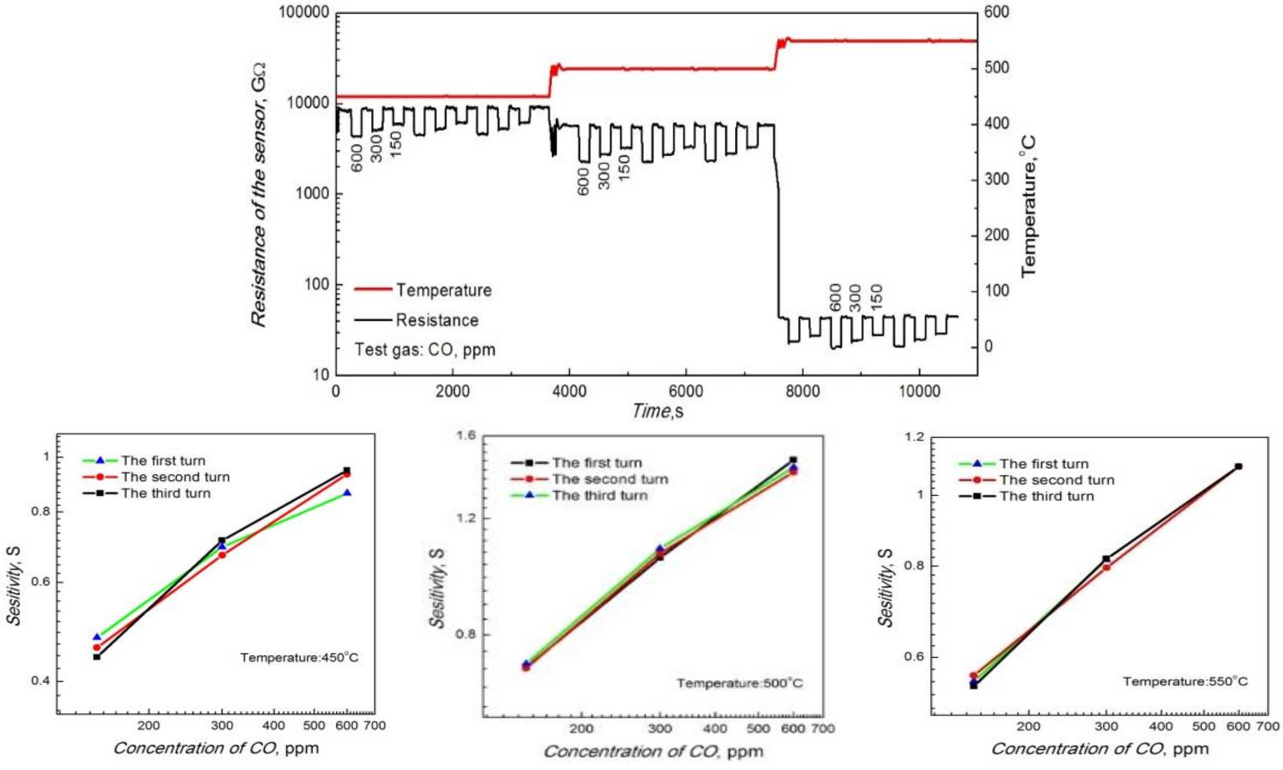

Fig.7 CO Sensing Curves and Sensitivity Curves of TiO_2 Gas Sensor at Different Temperature

The testing results is showed as Figure 7, the baseline of the gas sensor resistance in dry air is stable at different temperature. With the temperature increase, the sensor resistance will decrease. The injection of CO will cause obvious change of sensor resistance, and the repeatability is well. Defining the sensitivity of gas sensor as $S=R_a/R_g-1$, then sensitivity of gas sensor at different temperature and atmosphere can be determined as showed in Figure 7. The results show that the sensitivity of gas sensor is proportional to the concentration of CO in logarithmic coordinate, and the linearity is well, which indicating the TiO_2 sensor is excellent.

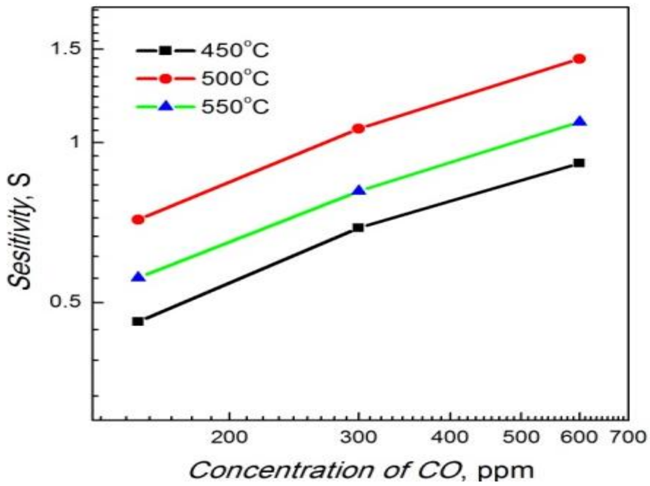

Fig.8 Sensitivity Curves of TiO_2 Sensor at Different Temperature

After some data processing, the sensitivity of TiO_2 sensor at different temperature can be got as Figure 8. Results show that the linearity of the sensitivity curves at different temperature is well. The maximum sensitivity is at the temperature of 500°C, and the minimum is at the temperature of 450°C, indicating that there is an optimal testing temperature for the TiO_2 gas sensor.

Conclusions

This paper prepare TiO_2 gas sensor for CO detection by stagnation flame synthesis directly, and test the sensing properties. Meanwhile, the characterization of the particles and film are also done to determine the properties of flame synthesis. Some conclusions can be got from the results.

Diameter of particles is mainly affected by the concentration of precursor, and higher concentration of precursor is benefic for producing larger particles. In the concentration range of 800ppm ~ 1000ppm, the particle diameter increases linearly with the concentration of precursor. With a fixed concentration of precursor, the growth rate of film is increasing first and then decreasing. At the time range from 60s ~ 120s, the growth rate is relatively stable. A TiO_2 gas sensor is prepared by stagnation flame synthesis directly. Testing results show that the linearity between the sensitivity and the concentration of precursor is well, indicating that the TiO_2 sensor is excellent. There is an optimal testing temperature, about 500°C.

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