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Pd-doped TiO_2 film sensors prepared by premixed stagnation flames for CO and NH_3 gas sensing

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ABSTRACT

This paper synthesized Pd-TiO_2 films by the flame stabling on a rotating surface (FSRS) technique with different doping ratios of Pd. The semiconductor metal oxide (SMO) particles together with Pd additive condensed in the post flame zone, and then deposited directly on a sensor subtract which is fixed on a rotating plant to form the sensing films. The composition and structure of sensing films were assessed with TEM, SEM, XPS, XRD and EDS techniques. It was found that TiO_2 particles prepared by the FSRS technique had diameters ranging from 9 to 17 nm and are in anatase type. Pd-doped TiO_2 films remained porous anatase and Pd element dispersed well in the TiO_2 film. The sensing test results showed that the nano film sensors synthesized by FSRS technique responded rapidly to CO concentration change while rather slowly to NH_3 concentration change. The doping Pd improved the response sensitivity of TiO_2 sensor remarkably for CO sensing, and a certain extent for NH_3. An optimal doping ratio existed and the TiO_2 film sensor sample with 1.0 wt.% Pd-doping ratio had the best gas sensing performance.

1. Introduction

Due to its wide band gap, chemical stability [1] and high porosity, titania (TiO_2), a semiconductor metal oxidation (SMO) is used as a gas sensor material to detect oxygen [2], flammable gases [3–5] and reduction gases [6–9].

Conventionally, the SMO films are fabricated by methods such as sol-gel [10] and hydrothermal [11,12], using the pre-made nano particles. The methods are indirect and required to follow a set of strict pre-procedures and post- procedures. Alternatively, flame synthesis is a direct method for nano-SMO sensor fabrication. In this method, the nano-particles formed in the post flame zone directly deposit on a sensor substrate to form a porous nano-SMO film. Among them, the Flame Spray Pyrolysis (FSP) process, which uses flame as heat source to decompose the liquid precursors carried by a gas jet, is often used [13]. It can quickly and cleanly produce highly porous thick films with a large accessible surface in one step. For example, Madler et al. [3] made Pt/SnO_2 films with FSP process and found that the sensors could exhibit a remarkably low detection limit of 1 ppm CO at 350 °C. Recently, H. Wang and his coworkers [5,14] proposed a nano-SMO sensor frabrication method called the flame stabilizing on a rotating surface (FSRS). It was found FSRS technique could fabricate pure TiO_2 sensing films with better sensitivity to CO than those made of P25 TiO_2 particles [5]. Miao et al. found FSRS technique could obtained TiO_2 sensing films with high stability and sensitivity to both CO and O_2, and their performances could be optimized by adjusting the critical influencing parameters [14]. Since it can also fabricate several sensors with reliable performance at one time, FSRS technique is regarded as an effective flame synthesis technique.

To improve the sensitivity and stability of SMO sensors, additives are also often doped into the SMO materials in the conventional frabrication processes. Ruiz et al. used sol-gel process followed by hydrothermal treatment to produce nanocrystalline TiO_2 and then doped the SMO particles with Au, Ag, Pt, Pd, Co and Cu respectively [1]. They found that TiO_2 crystal structure can be affected by the metal dopants. Doping Ag, Pt, Cu, Co, Nb and V atoms induce the transformation of anatase to rutile, but doping Au and Pd atoms do not. Mukhopadhyay et al. produced Pd-doped TiO_2 thin films by DC magnetron sputtering, and found that doping Pd

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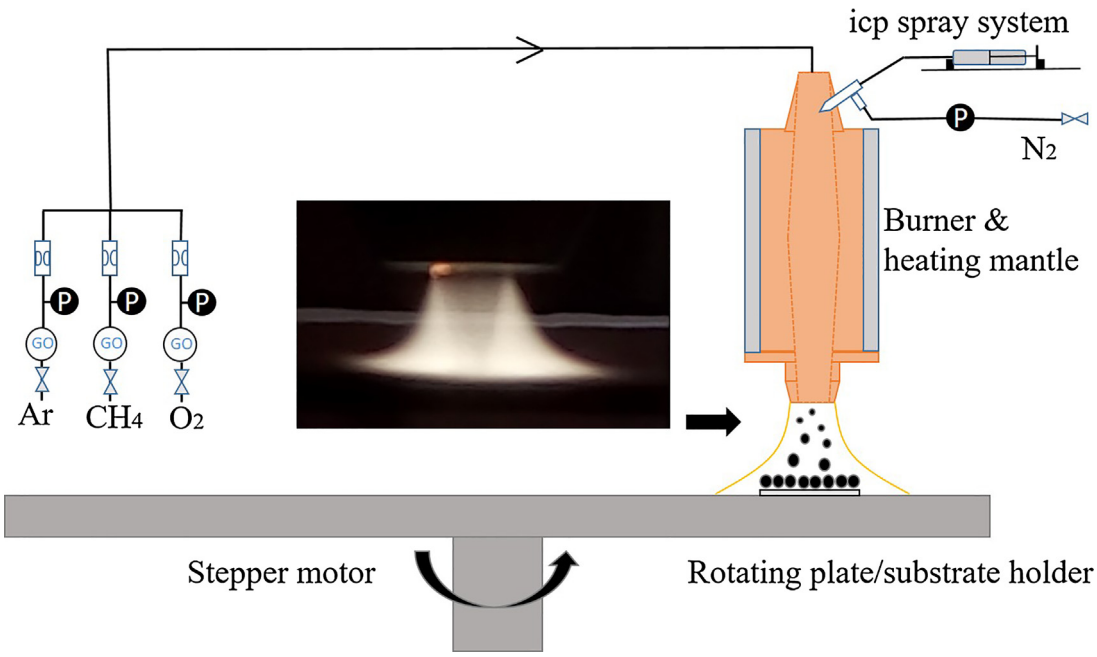

Fig. 1. FSRS synthesis system.

improved the NH_3 gas sensing sensitivity and lowered its operating temperature [15].

In fact, the flame synthesis method is more convenient for the additive-doped SMO sensors fabrication because it can handle additives doping in the synthesizing process and fabricate multi-component films with uniform additive dispersion in one step [16–18]. However, the existing studies on the additive-doped SMO sensors fabricated by flame synthesis were very few and they were limited to those using FSP process. The associated study using FSRS technique was not reported.

Consequently, in this study, FSRS technique was used to fabricate Pd-doped TiO_2 gas sensing films under various doping ratios. CO and NH_3 gases were chosen as the target gases in gas sensing tests for the potential application in detecting the flue gas compositions for automobiles and power plants. The components and micro-structure of the doping films were assessed to understand the mechanisms for the improvement of gas sensing properties caused by Pd-doping.

2. Experimental

2.1. Sensing film synthesis

TiO_2 gas sensing films were fabricated using FSRS technique. The synthesis system is schematically illustrated in Fig. 1. It consists of a gas supply unit, an ultra-fine spray unit, a burner, an electric heating mantle and a rotating plate.

The burner has an aerodynamically shaped nozzle with outlet diameter of 1.4 cm. The nozzle is placed off-centrally over a rotating plate, which is a stainless steel disc with 30 cm in diameter and 0.5 cm in thickness. The distance between the nozzle exit and the top surface of the disc is 2.0 cm. On the top surface of the disc, an array of alumina sensor substrates with an area of $8 \times 8\ mm^2$ were evenly affixed round a circle with a diameter of 13 cm. The sensor electrodes, made by gold films, were printed on the substrates. The active area of sensor electrodes is $4 \times 5\ mm^2$, and the width of the electrode is 100 μm, spaced by 100 μm.

The precursors used for SMO synthesis were prepared by dissolving a certain amount of palladium acetate and titanium tetraisopropoxide (TTIP) in xylene, with a volumetric ratio of 1:4. The film composition and additives are listed in Table 1. Before synthesizing, the precursors were stirred for 0.5 h to ensure the palladium acetate has been solved sufficiently. Then, the solution was fed into an inductively coupled plasma (ICP) atomizer by a syringe pump at the flow rate of 0.58 mL/min. After the solution was atomized, the precursors were carried by N_2 stream with a flow rate of 0.376 lpm (liter per minute) at a pressure of 2.0 atm to mix with the main gas stream in the mixing chamber of the burner. The main stream was a mixture of CH_4, O_2 and Ar, supplied at the flow rates of 2.2, 6.3 and 14.7 lpm, respectively. The mixing chamber was heated to 523 K to keep the atomized precursors being totally vaporized.

Table 1
Precursor ingredients.

Sensor	Film composition	$Pd(OAc)_2$ additive (g) in 6 mL TTIP
Sample 1	TiO_2	/
Sample 2	0.5 wt.% Pd/TiO_2	0.017
Sample 3	1.0 wt.% Pd/TiO_2	0.035
Sample 4	2.0 wt.% Pd/TiO_2	0.070
Sample 5	4.0 wt.% Pd/TiO_2	0.143

The precursors kept inactive until they reached the flame zone, where they rapidly decomposed. Since the surface of the rotating plate was cooled down by the air, there existed a large temperature gradient in the post flame zone. In the post flame zone, precursors and additives underwent nucleation and coagulation to form nano-particles. Driven by the thermophoresis force, the nano-particles rapidly deposit onto the sensor substrates to form porous films with integrated structure. As the deposition proceeded, the particle growth quenched, and their size kept in nano-scale.

To get stable gas sensing performance at high temperature, all films formed by flame synthesis were post-treated. In the post-treatments, particles deposited outside of the active area were cleaned and the films were sintered in a muffle furnace. In the sintering process, the furnace was slowly heated up from room temperature to 623 K with a rate of 2 K/ min. After the furnace was maintained at 623 K for 30 min, it was further heated up to 823 K and kept at that temperature for 5 h, and then was cooled down to the room temperature.