Sensors and Actuators B 144 (2010) 280–288

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Sensing properties of atmospheric plasma-sprayed WO_3 coating for sub-ppm NO_2 detection

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ARTICLE INFO

Article history:
Received 26 August 2009
Received in revised form 20 October 2009
Accepted 2 November 2009
Available online 13 November 2009

Keywords:
Tungsten oxide
NO_2 gas sensor
Atmospheric plasma spraying

ABSTRACT

Tungsten oxide (WO_3) sensitive layers for NO_2 sensors were fabricated by atmospheric plasma spraying technique followed by a heat-treatment. The phase structure and microstructure of the as-sprayed and heat-treated coatings were characterized by X-ray diffraction and scanning electron microscope. The sensing characteristics of these sensors were obtained by measuring the response towards NO_2 in moist air with a concentration in the range of 0–450 ppb and at a working temperature in the range of 95–240 °C. The results showed that the WO_3 coating prepared with low temperature plasma (Ar plasma) had a better sensitivity than the one deposited with high temperature plasma (Ar–H_2 plasma) due to a more porous structure. The obtained WO_3 sensors were found to exhibit different sensing behaviors depending on the working temperature and NO_2 concentration. The electrical resistance of WO_3 sensor increased at high NO_2 concentration in moist air and at a low working temperature. Whereas, it was found that the resistance decreased when the NO_2 concentration was lower than 93 ppb and the working temperature was higher than 130 °C.

1. Introduction

The detection of nitrogen oxides (NO_x: NO and NO_2) is important for monitoring environmental pollution resulting from combustion or automotive emissions [1]. Especially NO_2 is highly toxic to human nerves and respiratory organs so that high-sensitivity detection is desired for air quality monitoring. Commercially inexpensive, small size and maintenance-free solid state sensors for monitoring this gas are urgently needed. Semiconducting metal oxides such as tungsten trioxide (WO_3) and tin oxide (SnO_2) have been widely investigated for NO_2 detection [2,3]. WO_3 and WO_3 based oxide are important metal oxides for semiconductor gas sensors to detect non-hydrocarbon gases like NO_2 [4,5], H_2S [6–8] and NH_3 [9,10]. The NO_2 sensitivity has been shown to be improved by using fine particles of WO_3 [3,11] or thin films of WO_3 [12,13]. These results suggest that further improvements in NO_2 sensitivity may be possible by tailoring the microstructure of WO_3. The preparation of WO_3 coating has been tried by many routes, such as sol–gel [14–16], plasma-enhanced chemical vapor deposition [17], RF reactive sputtering [18,19], thermal evaporation [5,20], and pyrolysis [21,22]. It is important to note that the sensor response of WO_3 depends significantly on the preparation process [23]. Following this point, many works have been performed on the structural, electrical and sensing properties of WO_3 thin coatings [24–27]. These sensors have been reported to have good selectivity for low concentration NO_x.

Although the investigation on WO_3 sensitive layers has been conducted for a long time, it can be pertinent to indicate that the gas sensing properties of plasma-sprayed WO_3 coating were less investigated. In this article, WO_3 coatings were deposited by atmospheric plasma spraying process followed by a post-heat-treatment, and the microstructure of the as-sprayed and heat-treated coatings was examined. The response of WO_3 coatings to NO_2 was measured with various gas concentrations at different temperatures.

Atmospheric plasma spraying is a conventional coating preparation method [28]. It may also be a promising method to deposit WO_3 sensitive layers because of its high deposition rate, cost effectiveness and improved adaptability for automatic production. Plasma spraying is the most flexible among all the thermal spray processes due to using plasma as a heating source can provide sufficient energy to melt any materials which exhibit a congruent melting behavior. A high frequency plasma arc is ignited between an anode (nozzle) and a cathode. Plasma forming gases (generally mixtures of Ar and H_2) flowing between two electrodes is partially ionized to become a plume of hot plasma gas with the temperature of 6600 to 16,600 °C [29]. When the feedstock material is injected into the plasma, it is melted and simultaneously propelled towards the target substrate. Atmospheric plasma spraying process operates under air atmosphere without using controlled vacuum cham-

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0925-4005/$ – see front matter
doi:10.1016/j.snb.2009.11.006

ber promises fast coating production with potential automated lines.

Atmospheric plasma-sprayed coating is formed by a stream of total/partial molten droplets impacting a substrate. The individual droplet spreads to a thin lamella. The stacking of lamellae constitutes the coating. A plasma-sprayed coating is generally of lamellar structure. Pores are always present in the obtained coating. A fraction of voids from several percents up to 20% can be formed in the deposit [30]. Some of the voids result from insufficient filling and incomplete wetting of molten liquid to previously formed rough deposit surfaces. The microcracks can be formed easily in the splat of ceramic materials because of quenching stress that occurs in the splats. Such microcracks are also a kind of void that appears in the coating and constitutes a fraction of porosity. The voids in the deposits can generally be divided into three types on the basis of the dimension of voids, i.e., three-dimensional type, two-dimensional type and microcracks in ceramic deposits [31]. Three-dimensional type voids are similar in morphology to those in the materials processed by powder metallurgical method, and coarse voids in a size from sub-micrometer to more than 10 μm. Two-dimensional type voids correspond to the inter-lamellar gap (non-bonded interface between lamellae), and are in the sub-micrometer dimension perpendicularly to splat plane, but their sizes are comparable with the size of splat in the other two directions. Therefore, such voids present typically the “coin”-shape morphology. Because of the numerous coarse pores, inter-lamellae gaps and intra-lamellae cracks, as well as the small pores in the feedstock powders introduced to the as-sprayed coating by plasma spraying process, the coating can be very porous and be employed for applications in gas sensing. Moreover, the coating microstructure can be easily tailored by adjusting the in-flight particle velocity and temperature upon impact via the spraying parameters, e.g., arc current, Ar flow rate, H_2 flow rate, spraying distance, etc., which are directly numerically controlled.

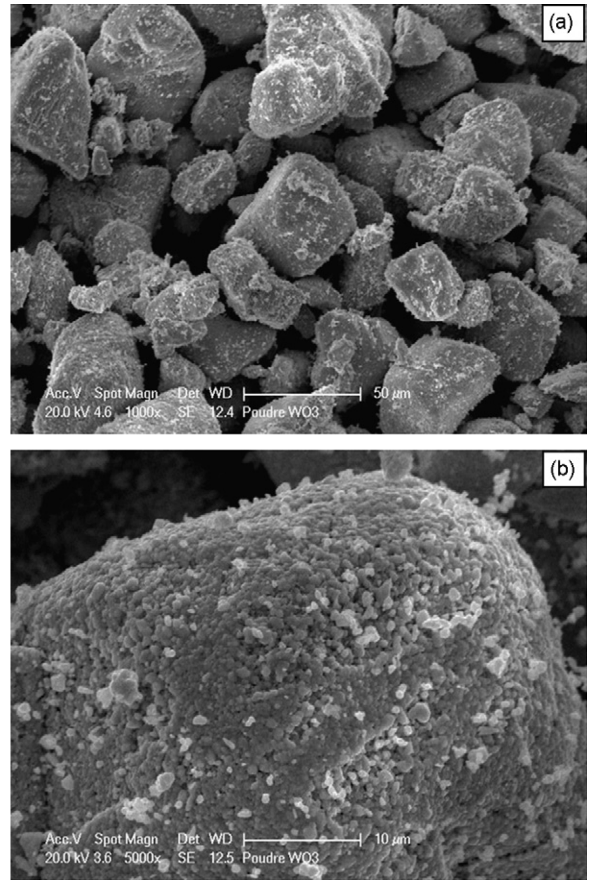

Fig. 1. Surface morphology of WO_3 powders: (a) low magnification (1000×) and (b) high magnification (5000×).

2. Experimental

To estimate the electrical properties of WO_3, it is necessary to use a substrate fitted with electrodes. It acts as a transducer. It is thus possible to measure the parameters that we want, namely the electrical resistance of the sensitive layer. The support is an electrical insulator made of a sintered alumina (Al_2O_3) plate. On the top view surface of Al_2O_3 plate, a pair of interdigitated gold electrodes is deposited by screen printing. As WO_3 coatings need to work at high temperature (typically 200–600 °C) to get a better sensing performance, a resistance heater made of platinum is also deposited by screen printing on the back of the Al_2O_3 plate and is covered with a protective layer. The gold electrode, the sintered alumina support and Pt heater (with the protective layer) constitute a substrate for subsequent WO_3 sensitive deposition. These substrates are fabricated by C-MAC Micro Technology Company (Belgium).

2.1. Feedstock powders and APS spraying parameters

A commercially available WO_3 powder (Sigma–Aldrich Chemie GmbH, Germany) is used as feedstock material for plasma spraying. Fig. 1a and b exhibits the morphology of the WO_3 powders with different magnifications. It is shown in Fig. 1b that the WO_3 powder is agglomerated with ∼500 nm small grains. The size distribution of the agglomerated powder is characterized by a laser diffraction apparatus (Mastersizer, Malvern Instruments Ltd., UK) as shown in Fig. 2. It shows a lognormal distribution with a particle size of 23.1 μm (d10), 43.6 μm (d50) and 77.5 μm (d90).

WO_3 coatings are deposited using a Metco A-2000 (Sulzer Metco AG, Switzerland) F4MB torch with 6 mm diameter nozzle on the designed substrates as shown in Fig. 3a. Prior to spraying, the substrate, the dimension of which is given in Fig. 3b, is cleaned by ethanol. During spraying, the WO_3 powders are fed by a Twin-System (Plasma-Technik AG, Switzerland) powder feeder. Ar with/without H_2 is used as plasma forming gas. A robot (ABB, Sweden) is used to move the spraying torch in order to achieve

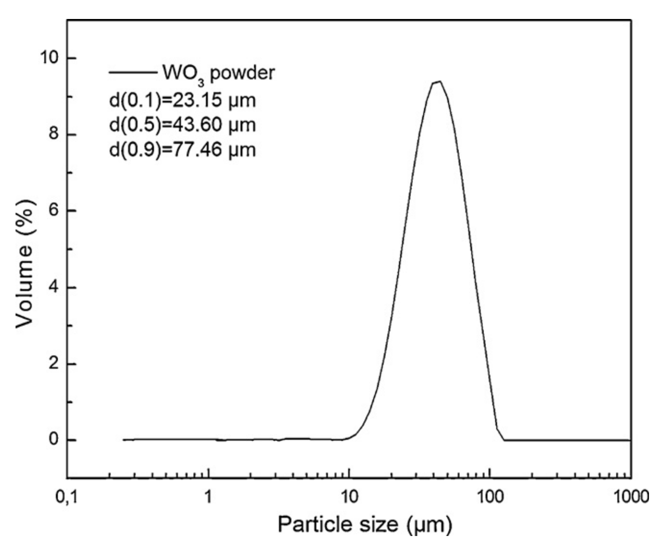

Fig. 2. Size distributions of the WO_3 powders.