Sensors and Actuators B 133 (2008) 687–693

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Sensing properties of chemically sprayed TiO_2 thin films using Ni, Ir, and Rh as catalysts

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ARTICLE INFO

Article history:
Received 4 October 2007
Received in revised form 31 March 2008
Accepted 3 April 2008
Available online 8 April 2008

PACS:
07.07.Df
73.61.–r
52.77.Fv
81.15.Rs

Keywords:
Gas sensors
Thin films
Titanium dioxide
Ultrasonic spray pyrolysis

ABSTRACT

The purpose of this work is double, to analyze the influence of (i) the addition of different catalysts and (ii) the implementation of different procedures to introduce them in the titanium dioxide (TiO_2) thin films, in order to improve the film sensitivity for detecting oxygen. For reaching these objectives, TiO_2 thin films were deposited on alumina substrates by the ultrasonic spray pyrolysis (USP) technique employing titanium(IV) oxide acetylacetonate ($TiO(acac)_2$) as a titanium precursor, and pure methanol as a solvent. Iridium, nickel, and rhodium were the three catalysts used, which were incorporated by impregnation and USP onto the TiO_2 thin films surface. The electrical characterization, consisting in surface resistance measurements of the films, in a mixture of oxygen and zero-grade air, was performed using interdigitated gold electrodes contacted on the alumina substrates. From these, the film response or resistance change of the TiO_2 films was estimated. Single TiO_2 thin films measured at 400 °C displayed a response of the order of 0.02 and 0.18 to oxygen of 1000 and 10,000 ppm, respectively, whereas TiO_2 thin films using impregnated rhodium proved to have the highest response to O_2, with a value in the order of 2.5 to a concentration of 1000 ppm of O_2 diluted in zero-grade air at an optimal operating temperature of 250 °C.

1. Introduction

As far as security and environmental protection are concerned, product specifications become more severe every day, thus requiring the development of highly sophisticated regulation and control systems. In this respect, the development of gas sensors, associated with microelectronic technology and data processing, allows the production of systems which can be used as alarms for gas detection or regulation. Among the many applications of gas sensors, the production of portable systems and the need and development of multifunctional sensor systems ("*electronic nose*") by means of a pattern recognition method require cheap sensor devices with low power consumption. The improvement of thin film gas sensors based on semiconducting metal oxides appears in this context as a possible answer, due to the full compatibility of the modern deposition techniques with microelectronic technology. Nowadays, it is possible to manufacture miniaturized gas sensors and, by using micromachining, to develop thermally isolated structures with low levels of power consumption. Moreover, the batch process fabrication assures good reproducibility and low cost.

The use of catalytic additives to improve the characteristics of solid-state gas sensors is a widely extended practice in both commercial and research fields [1,2]. Primary interest falls on increasing the efficiency of the catalysts. Consequently, additives are introduced seeking an increase of the sensing layer selectivity and sensitivity as well as the response velocity, and a decrease of the operation temperature.

Metal-oxide semiconductors are used in gas sensors applications due to the dependence of their electrical conductivity or resistivity on the ambient gas composition [3]. This phenomenon is based on two types of processes [4]. The first one involves bulk processes where the oxide defect chemistry balances the ambient oxygen pressure, determining the carrier concentration and consequently the bulk electrical conductivity. The second one involves surface processes where chemisorption of oxygen captures electrons from the oxide, producing a depletion region near the surface as well as increasing the surface conductivity. Semiconducting metal oxides, in general, and TiO_2, in particular, have attracted the attention of many users and scientists interested in gas sensing under atmospheric conditions.

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doi:10.1016/j.snb.2008.04.002

Titanium oxide is a native oxygen-deficient metal oxide containing donor-like oxygen vacancies and therefore is an n-type semiconductor [5]. It can present three different crystalline phases: brookite (orthorhombic), anatase, and rutile (both tetragonal) [6]. Rutile is a thermodynamically stable phase, while anatase and brookite irreversibly transform to rutile at high temperatures [7]. TiO_2 (rutile in most cases) is used for gas sensors, working at temperatures as high as 800 °C [8]. Conversely, anatase is less dense and less stable than rutile phase. TiO2 anatase thin films have been synthesized in our laboratory using the ultrasonic spray pyrolysis (USP) technique [9]. In this work we explore the gas sensing properties of the anatase phase TiO2 thin films. Un-doped TiO_2 thin films with well-characterized anatase structure present a significant and very rapid response to oxygen at relatively low temperatures ($375 \leq T \leq 425$ °C). The addition of catalysts such as iridium, nickel, and rhodium to the TiO_2 films makes them more sensitive to oxygen and modifies the response speed. The catalytic effect of these elements is based on their work function values, which are higher than the ZnO work function. Then, when a catalyst is present on the surface region, an accumulation of electrons will be generated along that region, which will increase the adsorption of different oxygen species, and consequently the surface resistance will increase.

2. Experimental procedure

2.1. Fabrication of the gas sensors

First of all, interdigitated electrodes were manufactured onto cleaned alumina substrates (sized 1.25 cm × 1.25 cm) by vacuum thermal evaporation of gold (99.999%, Aldrich) through a metallic mask. This was done in order to obtain a maximum specific area (surface area/volume ratio), which resulted in a spacing between the electrode fingers of approximately 1.1 mm with electrodes having a thickness of 1.5 μm. Fig. 1 shows the geometry of the electrodes. The washing process of the substrates consisted in a washed with trichloroethylene ($ClCH=CCl_2$, Baker) to degrease the substrate, followed by methyl alcohol (CH_3OH, Baker), and then in acetone (CH_3COCH_3, Baker). The three steps were performed in an ultrasonic bath with a duration of 5 min each. Finally, the substrates were dried by jet-propelled nitrogen gas (Praxair).

Afterwards, TiO_2 thin films were deposited through a stainless steel mask on the electrodes region by the USP technique,

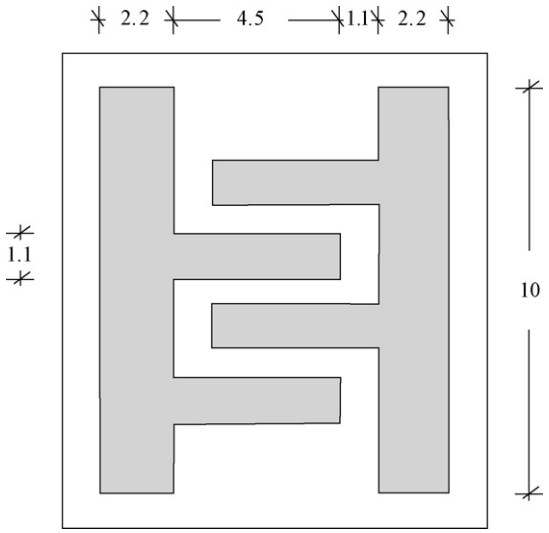

Fig. 1. Upper view of a sensor with an interdigitated electrode structure to measure the electrical resistance of the sensitive material (dimensions in mm).

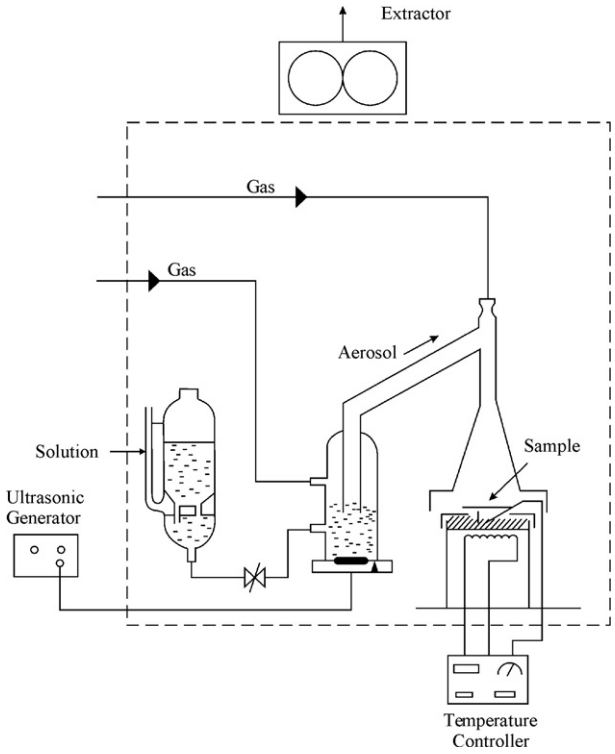

Fig. 2. Schematic diagram of the ultrasonic spray pyrolysis system used for the deposition of TiO_2 films.

leaving free from TiO_2 deposition the two main bars. USP technique constitutes a versatile technique able to produce nanoscale size powders and thin films. The particle size within these powders could be easily controlled by varying the concentration of the source solution and the atomization parameters. A schematic diagram of the USP system used is shown in Fig. 2. The starting solution was prepared by dissolving titanium(IV) oxide acetylacetonate ($TiO(CH_3COH=C(O^-)CH_3)_2$, Aldrich) in pure methyl alcohol (CH_3OH, Baker) at a 0.05 M concentration. The deposition system used contains a piezoelectric transducer operating at variable frequency, which was set to 1.2 MHz, and an ultrasonic power of 120 W, using a substrate temperature (T_s) of 450 °C within an accuracy of ±1 °C. Filtered atmospheric air was used as carrier and director gas, with air flow rates of 3.5 and 0.5 l min^{-1}, respectively, within an accuracy of ±0.05 l min^{-1}. The deposition time was set to 7.0 min.

2.2. Incorporation of catalysts on the TiO_2 thin films

Firstly, un-doped TiO_2 films with a thickness in the order of 220 nm were produced under optimal preparation conditions in order to have a reference for comparison of the characterization results. Secondly, catalysts were added to these. The catalysts (Ir, Ni, and Rh) were incorporated on the surface of the active TiO_2 film by two different methods. The first one consists in the impregnation of the TiO_2 thin films, previously deposited on the alumina substrates, from a chemical solution containing the particular catalyst. The starting solutions containing the different catalysts were separately prepared maintaining a fix concentration at 1.55×10^{-4} M of, iridium (III) acetylacetonate ($((CH_3COCH=C(O^-)CH_3)_3Ir$), nickel (II) acetylacetonate ($Ni(C_5H_7O_2)_2$), and rhodium (III) acetylacetonate ($((CH_3COCH=C(O^-)CH_3)_3Rh$), all of them from Aldrich. The TiO_2 films were impregnated with the respective solutions by applying a hundred of brushstrokes by the "*paint on*" method, using a brush, and since the solvent in which the catalysts were suspended