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ScienceDirect
Sensors and Actuators B 128 (2008) 407–413
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Sol–gel derived TiO_2:ZrO_2 multilayer thin films for humidity sensing application

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Received 13 April 2007; received in revised form 25 June 2007; accepted 26 June 2007
Available online 1 July 2007

Abstract

In the present work, we describe humidity sensing properties of nano-structured multilayered TiO_2:ZrO_2 ceramic thin films prepared by sol–gel processing. An enhancement in the sensitivity is observed for both TiO_2/ZrO_2 (TZ) and ZrO_2/TiO_2 (ZT) thin film samples that are annealed at 400 °C, due to simultaneous crystallization of ZrO_2 and TiO_2. The multilayered ZrO_2:TiO_2 thin film shows less drift and low hysteresis compared to pure TiO_2. The experimental data are fitted to an equivalent circuit containing a resistance and a non-Debye capacitance in parallel. Typical response and recovery time of the sensor are 56 and 124 s, respectively. We demonstrate the possibility of a practical device without heating the humidity sensitive element for regeneration.

Keywords: Humidity sensor; Sol–gel; Multilayered structures; Stability

1. Introduction

The measurement and control of humidity in air or other gases is important in many areas such as meteorology, domestic environment, medical equipment, food production, and industrial and agricultural processes. Ceramic humidity sensors have been widely used because of their advantages when compared to the polymeric ones, principally arising from an improved thermal, chemical and mechanical stability [1,2]. Most of the commercial ceramic humidity sensors are based on changes in impedance of porous-sintered oxides at different environmental humidities. The impedance changes of the ceramics with humidity are related to the water adsorption mechanism on the oxide surface. At low relative humidity (RH), conduction is due to proton hopping between hydroxyl ions on the first layer of chemisorbed water, while at high RH, protons hop between physisorbed molecules, with a charge transport by a Grotthuss chain reaction [1]. The presence of capillary pores permits the condensation of adsorbed water, resulting in an electrolytic conduction which is added to protonic conduction. Moreover, thin film materials offer shorter response and recovery time than bulk ceramics.

The desirable characteristics of humidity sensors are high sensitivity, low hysteresis, short response and recovery time, low cost, and excellent stability for a long time. So far however, there has not been any optimum material that can simultaneously fulfill all of these requirements [3]. One of the major problems of a ceramic humidity sensor is the progressive drift in resistance of the ceramic sensor, which is caused by the gradual formation of stable chemisorbed OH^- on the oxide surface by the prolonged exposure to humid environment. Given the ionic-type humidity sensing mechanism, the proton hopping is adversely affected by the surface presence of hydroxyl ions instead of water molecules, thereby resulting in a decrease in surface conductivity [2]. It is possible to remove the adsorbed hydroxyl ions by periodic regeneration before each operation. The hydroxyl ions are removed by heating to temperatures higher than 400 °C for a short period of time [4]. The higher temperature heat treatment results in an increase in the power consumption of the device.

Nano-structured thin films are optimal candidates for humidity sensing due to the high surface area that facilitates the adsorption process of water. ZrO_2 and TiO_2 thin films have been prepared by several techniques, which include sputtering, chemical vapor deposition, pulsed laser deposition and sol–gel process [5–8]. Of these processes sol–gel deposition has

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doi:10.1016/j.snb.2007.06.029

attracted much interest due to the excellent compositional control, and homogeneity at the molecular level due to mixing of liquid precursor and lower crystallization temperature. Moreover, the microstructure of the thin films deposited by sol–gel process can be tailored by the control of processing parameters [9]. Both TiO_2 [10–13] and ZrO_2 [14] are widely reported materials for gas as well as humidity sensing. Among various phases of TiO_2, anatase phase is reported to be the best for humidity sensing properties due to the higher water adsorption capacity of this phase [15]. Additionally, physisorbed water is easy to desorb from the anatase phase in comparison to the rutile phase as reported by Egashira et al. [16]. Chow et al. [11] have reported that hysteresis can be reduced by controlling the anatase to rutile ratio in the TiO_2 thin films.

There has been an increasing interest on the multilayered humidity sensor as reported by several authors. Humidity sensors having bilayered structure like TiO_2/SnO_2 [17], TiO_2/Al-doped ZnO [18], and ZrO_2/SnO_2 [19] have been reported. The advantage in using bilayered structure is that it offers less hysteresis than single layered structures. In the present work, nano-structured multilayers of ZrO_2/TiO_2 (ZT) and TiO_2/ZrO_2 (TZ) thin films were prepared by a sol–gel process. The humidity sensing behavior of the multilayered films, sintered at different temperatures, was investigated. In addition to low hysteresis, we observe an increased chemical stability in the multilayered structures when compared to single layered structures, i.e., multilayered films undergo less drift. The films have been characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). Electrochemical impedance spectroscopy (EIS) measurements have also been carried out for these thin films and the experimental data have been fitted with an equivalent circuit.

2. Experimental details

The titania sol was prepared by dissolving titanium isopropoxide (TTIP) in ethanol (C_2H_5OH). Water was added for hydrolysis and poly-condensation, and nitric acid was added to control the precipitation. The mixed solution was stirred at room temperature and 50–60% relative humidity (RH) for 5 h. The transparent solution obtained was then aged for 48 h and directly used for the preparation of the films. 0.2 M TiO_2 sol was prepared by using 1.5 ml TTIP, 0.15 ml HNO_3, 0.25 ml H_2O, and 24.5 ml ethanol. 0.1 M Zirconia sol was prepared using zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$) and ethanol as the solvent [8]. The sol was aged at 30 °C for 3 days. The films were deposited on alkali-free glass and alumina substrates using spin coating in air of 57–62% RH and a speed of 3000 rpm. Three layers of ZrO_2 and three layers of TiO_2 were deposited in an alternate manner. In TZ, ZrO_2 is the bottommost layer; while in ZT, it is TiO_2. The total thickness of the film was 200 nm as measured by cross-sectional SEM. The intermediate drying between successive coatings was done at 200 °C for 10 min and final calcination were done at different temperatures for 60 min in air. Thermal analysis of the dried gel was performed using TGA (PerkinElmer TGA-6) and DSC (Netzsch DSC 200 Phox) to identify the evaporation, decomposition and phase crystallization steps during pyrolysis. Samples were heated at a rate of 10 °C/min in flowing air environment. Thin film XRD measurements have been carried out using Philips X'Pert Pro with Cu Kα radiation and a gracing angle 2°. The surface morphology of the film was analyzed by SEM (Hitachi S-4800). The structural and humidity sensing studies have been carried out for the thin film samples which were annealed at various temperatures ranging from 300 to 550 °C for 60 min in air. After sintering at various temperatures, an inter-digital capacitor pattern of dimension 1.2 cm × 1.2 cm was formed on the surface of the thin films by evaporating gold (thickness 100 nm) through a mask. Different relative humidities were obtained with saturated aqueous solutions of salts; LiCl (11%), $MgCl_2$ (33%), NaBr (56%), NaCl (75%), and K_2SO_4 (97%). Sensor impedance was measured over the frequency range 5 Hz to 13 MHz using a Hewlett Packard impedance analyzer (HP Model 4192). In order to avoid Joule heating, low signal amplitude, i.e., 100 mV was used for all measurements. The experimental data were fitted using an equivalent circuit [20].

3. Results and discussions

Fig. 1a shows TG/DSC curves of TiO_2 xerogel. A total weight loss of about 25% was observed up to a temperature 350 °C, beyond which there was no noticeable weight loss. One can observe two well-defined regions for the weight loss; one below 200 °C and another from 200 to 350 °C. At temperatures below 200 °C, the weight loss is due to evaporation of water and organic solvents and also due to thermal decomposition of organic complexes. Between 200 and 350 °C, the weight loss is attributed to the combustion of organic constituents in the sol. The DSC result shows an endothermic peak at 113 °C, corresponding to the evaporation of water, and an exothermic peak at 210 °C due to combustion of the organic precursor. A large exothermic peak has been observed at 373 °C, which can be associated with crystallization of TiO_2. Fig. 1b shows TG/DSC plots of ZrO_2 xerogel. The weight loss of 50% from 30 to 400 °C is attributed to evaporation of the residual organic solvents and decomposition of the organo-zirconium compounds that had formed via hydrolysis and condensation during the preparation of the precursor sol. The DSC results show an endothermic peak at 127 °C corresponding to the evolution of water and organic solvents. A weak exothermic peak at 466 °C corresponds to the bulk crystallization of the gel powder [8].

Fig. 2 shows the XRD pattern of the TiO_2/ZrO_2 multilayer sintered at different temperatures. When the sintering temperature is increased to 375 °C, anatase TiO_2 phase starts appearing. There is no reflection corresponding to the ZrO_2 phase. As the temperature is further increased to 400 °C, the reflection from tetragonal ZrO_2 phase also starts appearing. It has also been observed that both ZrO_2 and TiO_2 reflections become sharper as the temperature increases, and the full width at half maximum (FWHM) decreases with an increase in temperature. With the increase in sintering temperature, the average crystallite size increases, resulting in greater crystallinity. The average crystallite size was calculated from the FWHM of diffraction line (1 0 1)