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Original research article

An investigation in to the impact of Ti doping on the structural, optical and sensing properties of spray deposited nanocrystalline ZrO_2 thin films

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ABSTRACT

Pure and Ti doped ZrO_2 thin films were prepared by chemical spray pyrolysis method on a glass substrate at 450 °C. XRD results reveal that pure and doped films had polycrystalline structure in nature with tetragonal phase and highly oriented along (011) plane. The crystallite size was increased with increasing Ti content from 17.6 nm to 25.3 nm. SEM images of ZrO_2 and ZrO_2:Ti thin films showed that the surface seems relatively homogeneous, and the EDX spectra confirm the stoichiometry of the prepared films. AFM measurements showed that the average roughness values were increased after doping with Ti. Optical transmittance of the deposited films high value was about (50%) and decreased with increasing of dopant concentration. The optical band gap decreased from 4.30 eV to 3.01 eV with increasing of Ti content. The ZrO_2 and ZrO_2:Ti (8%) thin films were investigated as NO_2 gas sensor, the results showed a maximum response was at 250 °C and had a stable behavior for detecting NO_2 gases. The doped ZrO_2 film illustrated a higher response than that of the pure film. The sensing mechanism was modeled according to the oxygen–vacancy mode.

1. Introduction

Zirconium oxide ZrO_2 is a very interesting material because of their applications that stand out stiff resistance for weather conditions since it combines between excellent mechanical toughness and corrosion resistant [1]. The ZrO_2 has three polymorphs, cubic, tetragonal and monoclinic phases. The monoclinic phase is thermodynamically stable near room temperature, while at higher temperatures tetragonal and then cubic phases become stable [2,3]. The temperature induced phase transitions from monoclinic to tetragonal and from tetragonal to cubic ZrO_2, were observed at 1205 °C (1478 K) and 2377 °C (2650 K) [4,5]. Its applications include fuel cells, thermal barrier coating, and protection against the corrosion of nuclear fuel cladding in water-cooled nuclear reactors. Furthermore, zirconia I used in biomedical hip implants, dental restorations [6–8]. Recently the semiconductor industry has begun using zirconia as a substitute for SiO_2 in MOSFET gate dielectrics [9,10]. The importance of environmental gas monitoring is well understood, and much research has been focused on the development of suitable gas sensitive materials recently, there has been considerable interest in exploiting substances for this purposes such metal oxides. The ZrO_2 thin films have been successfully fabricated using various technologies, sol–gel route by spin coating method [11,12], solution combustion method [13], atomic layer deposition [14,15], pulse laser depo-

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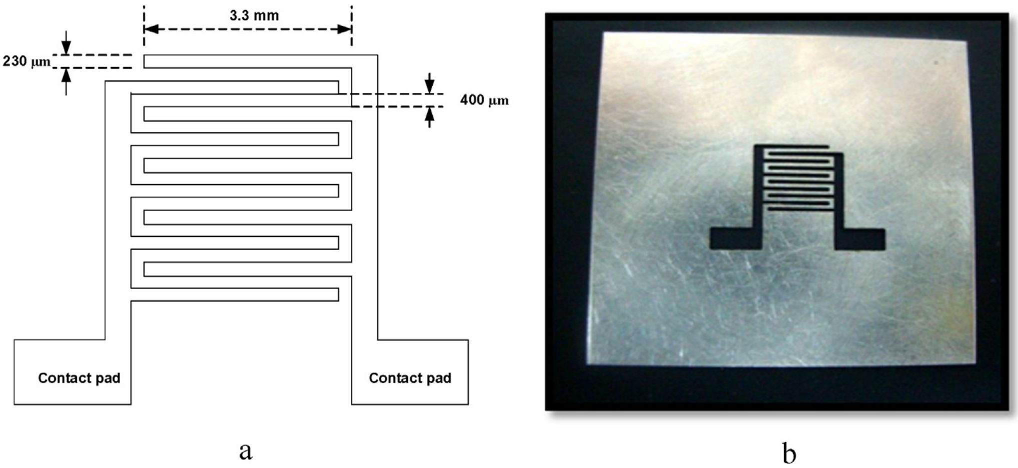

Fig. 1. a. Schematic diagram of gas sensor mask, b. Fabricated Al metal mask electrode.

sition PLD [16], RF magnetron sputtering [17], dip coating in sol-gel solution [18,19], spray pyrolysis and ultrasonic spray pyrolysis method [20,21]. Spray pyrolysis has been widely used to produce thin films because it is inexpensive method, then it is more economic than other (such as chemical vapor deposition and sol–gel) which involve multiple steps or that must be carried out under vacuum. Furthermore, spray pyrolysis offers numerous possibilities for controlled synthesis of advanced ceramic powders and films because of its chemical flexibility [22,4,5]. Therefore, the present work intends to investigate the effects of Titanium doping on the structural, optical and NO_2 gas sensing properties of spray deposited nanocrystalline ZrO_2 thin film.

2. Experimental part

2.1. Materials and synthesis of pure and Ti doped ZrO_2 thin films

ZrO_2 and ZrO_2:Ti thin films were prepared on glass substrates by chemical spray pyrolysis method at temperature of 450 °C, inorganic precursor route was chosen for the fabrication of nanocrystalline transparent zirconia thin films. 0.1 M precursor solution of Zirconium oxy chloride octahydrate $ZrOCl_2{\cdot}8H_2O$ provided from Fisons Co. was prepared by dissolving 8.05627 gm of $ZrOCl_2{\cdot}8H_2O$ in 250 ml of distilled water. The solution was sprayed onto preheated microscope glass substrates at 450 °C with dimensions of 2.5 × 2.5 cm^2 after it ultrasonically cleaned in acetone and Methyl ethyl ketone (C_4H_8O). Each spraying period lasts for about 12 s followed by about 3 min waiting period to avoid excessive cooling of the hot substrates duo to the spraying. Amount of 0.1 M of $TiCl_3$ provided from HR-200A&D Co. solution was added with volume ratios to $ZrOCl_2$ solution to get 4%, 8%, 12% of Ti doped ZrO_2 thin films.

2.2. Fabrication of gas sensors

Sensors were fabricated for pure and 8% Ti doped ZrO_2 thin films by chemical spray pyrolysis on glass substrate heated at temperature 450 °C. Al electrodes (300 nm thickness) were deposited by thermal evaporation in vacuum technique (Edward 306-Thermal Evaporation Coating Unit) using aluminum wire with purity (99.9%) Spiral Tungsten (w) boat and under pressure, 10^{-7} mbar as shown in Fig. 1.

2.3. Characterization

The crystal structure of ZrO_2 and ZrO_2:Ti films were characterized by X-ray diffractometer (Model-XRD- 6000 Shimadzu) using CuKα (λ = 1.54,056 Å) radiation. The surface morphology of the films was investigated by scanning electron microscopy (INSPECT-550) and atomic force microscope (CSP model AA3000 AFM supply by Angstrom Company). UV–vis (UV-1650 Shimadzu) spectrometer was used to determine the optical properties of the prepared films in the wavelength range (250–1100) nm. Electrical and gas sensing properties were measured using a local assembled gas sensing system as shown in Fig. 2. The sensor performance to exposure of NO_2 was examined.