INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 42 (2017) 4597–4609

Available online at www.sciencedirect.com

ScienceDirect

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

Custom designed metal anchored SnO_2 sensor for H_2 detection

Md. Shahabuddin [a], Ahmad Umar [b], Monika Tomar [c], Vinay Gupta [d,*]

[a] Department of Physics, Allama Iqbal College, Magadh University, Bodh Gaya 824234, India
[b] Department of Chemistry, College of Science and Arts, Najran University, Najran 11001, Saudi Arabia
[c] Department of Physics, Miranda House, University of Delhi, Delhi 110007, India
[d] Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

ARTICLE INFO

Article history:
Received 9 August 2016
Received in revised form
30 November 2016
Accepted 13 December 2016
Available online 11 January 2017

Keywords:
Semiconducting SnO_2
Spill over
EDR
EDZ
UTMCs

ABSTRACT

Herein, we report sputter deposited SnO_2 thin film based sensor structures anchored with different metal clusters (Pt, Au, Cu, In, W and Cr) for efficient detection of H_2 gas. Controlled decoration of ~9 nm thin Pt clusters having 200 μm dia on the top surface of SnO_2 thin film exhibited dramatically outperformed results. The Pt/SnO_2 sensor shows an improvement upto two orders in sensing response S~1.68 × 10^2 towards 500 ppm of H_2 gas at a relatively low operating temperature of 110 °C. The sensor exhibited excellent gas sensing characteristics in the concentration range 2–5000 ppm H_2 at operating temperatures of 70–230 °C. The sensor revealed negligible cross sensing signals against other interfering gases like acetone, IPA, TCE, NO_2, methane, LPG, petrol and NH_3. The structural and surface morphological studies of SnO_2 thin films were carried out. Reliability analysis and selectivity demonstration by Pt/SnO_2 sensor was found to be consistent over long term. The work envisions towards realization of targeted H_2 detection system at low temperature.

Introduction

Recently, development of cost effective, highly-sensitive, novel-designed and low temperature operated gas sensors based on simple fabrication technique has drawn considerable attention. A low power operated sensor with excellent sensing properties is of critical importance and is seriously required. Owing to unique property and outstanding functionalities, SnO_2 has been investigated extensively for potential applications in optoelectronic devices [1–3], rechargeable Li-ion batteries [4–6], gas sensors [7–9], bio-sensors [10,11] catalyst for oxidation of organic compounds [12,13], solar cells [14,15], electro-chromic windows [16,17]. SnO_2 is the most preferred material for gas sensing application due to its high electrical conductivity (~10^2 Ω^{-1} cm^{-1}) and natural tendency to adsorb oxygen on its surface. The high sensitivity, fast response, quick recovery and noble stability towards various target gases have made SnO_2 an extremely discriminating choice for sensing applications. It is widely used for environmental monitoring, food safety, security and optimal process control [18–20].

Conductometric gas sensors are ideal for their high sensitivity, low production costs, miniature sizes and simple configuration [21,22]. Since gas sensing is a surface phenomenon based on the change in surface conductivity and leading to the change in resistance on exposure to gases, so thin film sensing element is advantageous [23,24]. In SnO_2 films, oxygen

* Corresponding author.
E-mail addresses: shahmd42@yahoo.com (Md. Shahabuddin), drguptavinay@gmail.com (V. Gupta).
http://dx.doi.org/10.1016/j.ijhydene.2016.12.054
0360-3199/

vacancies are the inherent property. In ambient air, adsorption of oxygen molecules on the sensing layer causes trapping of electrons from the conduction band of SnO_2 and creates electron depleted regions near the surface or grain boundaries. The gas response characteristics (sensitivity, selectivity, response time and recovery time) strongly depend on the catalytic additives, structure of the sensing layer (crystallite dimension, porosity, stoichiometry of inter-crystalline barriers etc.) and different valence states of oxygen species (O_2, O^-, O^{-2}) [25,26].

Since last few years, H_2 is under significant attention of scientific communities due to ever growing demand of energy [27,28]. It has potential applications in fuel cells, nuclear power plants, industry, refining in petroleum products and space applications. It is highly explosive (minimum ignition energy ~0.017 mJ) in air at concentrations range ~4% [29–32]. Thus safety is the key concern to counter the explosion possibility due to accidental H_2 outflow at early step. A highly reliable and supersensitive sensor is in demand to detect H_2 gas of wide concentration range at low operating temperature.

Here, some reports on H_2 gas sensing based on SnO_2 thin films grown by various techniques are available [19,20,33–35]. Various catalysts and modifiers have been incorporated into the sensing material for detection of H_2 gas at low operating temperature [34–45]. Despite the promising developments in chemoresistive sensors, most of the reports show either detection of higher concentration of H_2 or poor sensitivity or higher operating temperature or long response time [20,34,40]. Surface activation by metal clusters is an efficient approach to improve sensing performance. Chowdhuri et al. [46] and Haridas et al. [47] used CuO and Pt clusters respectively at the top surface of sputtered SnO_2 thin film for enhanced gas sensing performance and now it has become a custom choice for other researchers too [48–50].

Sputtering is the standard and viable technique for producing high quality reproducible films. The objective of the present work is to develop RF sputtered SnO_2 thin film based H_2 gas sensor having detecting capability of wide concentration range at low operating temperature. To improve sensing properties, ultra-thin metallic clusters (UTMCs) to atop of SnO_2 thin film has been loaded and studied. Amongst all the sensors, Pt/SnO_2 sensor found exhibiting excellent sensing performance towards H_2 gas at 110 °C. Low detection limit of 2 ppm, rapid response and speedy recovery, excellent selectivity and no ageing effect speaks its novelty. When compared with results reported on H_2 sensors prepared by sputtering technique, the Pt/SnO_2 sensor is found worthy due to superior sensing properties [51–56]. Importantly, this technique for sensor fabrication is also compatible in designing of nanosensors for multiple gas sensor collections.

Experimental details

Sensor fabrication

SnO_2 thin films of 55 nm were deposited using RF magnetron sputtering technique onto a pair of comb-like platinum (Pt) interdigitated electrodes (IDEs) patterned over the corning glass substrate. The Pt IDE_s were patterned on the corning glass substrate using conventional photolithography technique and details has been explained elsewhere [57]. The deposition parameters used for growth of SnO_2 thin films are presented in Table 1. Initially the sputtering chamber was evacuated to a base pressure of 1.0×10^{-6} T and successively the reactive gas ((argon (ar) and oxygen (O_2) mixed) was inserted through MFCs to achieve the desired pressure. In order to achieve the preferred morphology of sensing layer and stable sensor resistance, the oxygen content in the reactive gas composition was varied over the range 40–60% and sputtering pressure was varied from 8 to 16 mT. During deposition, substrates were kept fixed at a distance of 13.5 cm from a 6 inch dia tin (Sn) target. An RF power of 200 W was applied to the target and films were deposited at room temperature. All as-grown SnO_2 thin films were found to be amorphous which were subjected to a post deposition annealing treatment at 300 °C for 2 h in air ambient in order to make crystalline and stabilize the film resistance. The SnO_2 thin film deposited with 50% ar and 50% O_2 content at a sputtering pressure of 10 mT showed a high sensing response and stable resistance and therefore these parameters were considered as optimized processing condition.

To achieve improved sensing response characteristics, the ultra-thin clusters (UTCs) of various metal catalysts i.e. platinum (Pt), gold (Au), copper (Cu), indium (In), tungsten (W) and chromium (Cr) were loaded to atop of SnO_2 thin films. Fig. 1 represents the schematic of Pt IDEs and SnO_2 thin film surface anchored with ultra-thin metallic clusters (UTMCs). The ultra-thin clusters (UTCs) of Pt, W and Cr were deposited by RF magnetron sputtering using their respective metal targets (purity 99.999%) in pure argon ambient while UTCs of Au, Cu and In were thermally evaporated. UTMCs of 9 nm thicknesses were loaded using a stainless steel (SS) shadow mask having uniformly distributed pores of 200 μm diameter. The sensor without metal catalyst is referred as bare SnO_2 whereas other sensors having UTCs of Pt, Au, Cu In, W and Cr are referred as Pt/SnO_2, Au/SnO_2, Cu/SnO_2, In/SnO_2, W/SnO_2 and Cr/SnO_2 respectively.

The crystallographic orientation and the optical properties of SnO_2 thin films were characterized using X-ray diffractometry (XRD (Discover, Bruker D8)) with CuK_α radiation. The surface roughness and morphology of films were studied using both high resolution field emission scanning electron microscopy (FESEM, (FEI Nova Nano SEM 450) and (Mira 3, TESCAN USA) and atomic force microscopy (AFM) in contact

Table 1 – Processing condition for the deposition of SnO_2 thin film.

Technique	RF magnetron sputtering
Substrate dimension	(1.5×1.5) cm^2
Target (T)	Tin (99.999%), 6″ dia.
Substrate (S)	IDE_s/corning glass substrate
T-S distance	13.5 cm
Base pressure	1.0×10^{-6} Torr
Deposition pressure	10 m Torr
Substrate temperature	Room temperature
Gas composition	50% argon: 50% oxygen
RF power	200 W