Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 409–415

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Nanostructured TiO_2 films: Enhanced NH_3 detection at room temperature

P. Dhivya[a], Arun K. Prasad[b], M. Sridharan[a,*]

[a]*Functional Nanomaterials & Device Lab, Centre for Nanotechnology & Advanced Biomaterials and School of Electrical & Electronics Engineering, SASTRA University, Thanjavur 613401, India*

[b]*Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India*

Received 27 May 2013; received in revised form 10 June 2013; accepted 10 June 2013
Available online 24 June 2013

Abstract

The influence of substrate bias on the ammonia (NH_3) sensing properties of reactive dc magnetron sputtered titanium dioxide (TiO_2) films has been investigated. The films deposited at floating potential and −100 V substrate bias exhibited a mixed phase (anatase and rutile) as analysed by X-ray diffraction (XRD) while the films deposited at −200 V substrate bias had only rutile phase. On increasing the substrate bias voltage the grain size increased from 15 to 31 nm and the optical band gap value decreased. The TiO_2 films had an enhanced response towards NH_3 in the concentration range 5−100 ppm at room temperature. The enhanced performances are correlated to the high surface-to-bulk ratio and crystal structure. The TiO_2 film deposited at lower bias has enhanced sensitivity of (S-7857) towards NH_3 at room temperature with quick response and recovery time.

Keywords: A. Films; D. TiO_2; E. Sensors; Sensitivity

1. Introduction

Ammonia (NH_3) plays a vital role in all forms of life and it is generally produced by the way of natural process in animals, human and plants. In addition to this, NH_3 is synthesized artificially due to its variety of applications in the field of explosives production, fertilizers, pesticides, textile, food processing, household cleaning and bleaching products. Although the threshold value for NH_3 concentration in air is 25 ppm for human being, above 25 ppm concentration of NH_3 it causes irritation to the respiratory system, eyes and skin and long term exposure of NH_3 leads to fatal [1]. Hence, there is a necessity for developing cost effective, reliable NH_3 sensors to detect in lower ppm with excellent performance. Various metal oxides are being used to detect NH_3 such as ZnO [2,3], WO_3 [4,5], TiO_2 [6,7], SnO_2 [8,9], etc. Among all sensors, room temperature based ammonia sensors can offer cost-reduction because of its reduced working temperature, low power consumption of sensor, miniaturized size and improved sensor life time. TiO_2 is an inexpensive, non-toxic and wide band gap n-type semiconductor. TiO_2 has high thermal stability, photocatalytic activity, chemical stability and high corrosion resistance [10]. The superior dielectric properties of TiO_2 meets the demand in ultra large scale integration, used as an alternative dielectric to silicon dioxide [11]. These features make TiO_2 as one of the potential candidates for gas sensing application.

Different deposition techniques such as, chemical vapour deposition [12], dip coating [13], spin coating [14], spray pyrolysis [15], magnetron sputtering [16], etc., are used to deposit TiO_2 films. Among all these techniques, dc magnetron sputtering has an advantage of controlling film thickness, uniform large area coating, well adherence of the film over the substrate, allows growth of films under a reactive atmosphere and avoids contaminants in the films during the deposition process. By changing the deposition conditions like partial pressure of argon, partial pressure of oxygen, substrate bias voltage, cathode power, substrate to target distance, deposition temperature, one can tailor the properties of TiO_2 films.

In this present work, TiO_2 films has been deposited by reactive dc magnetron sputtering and the influence of substrate

*Corresponding author. Tel.: +91 4362 304000x2277; fax: +91 4362 264120.
E-mail address: m.sridharan@ece.sastra.edu (M. Sridharan).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.06.016

bias on their structural, optical, morphological properties and NH_3 detection at room temperature are studied.

2. Materials and methods

2.1. Film deposition

TiO_2 films were deposited by reactive dc magnetron sputtering on to thoroughly cleaned microscopic glass substrates (1×1 cm^2). The illustrative representation of deposition chamber is shown in Fig. 1. The glass substrates were ultrasonically cleaned in acetone, isopropanol and deionized water (15 min in each solution). Subsequently, the substrates were dried in oven for 1 h. The well cleaned substrates were placed on to the substrate holder and the deposition chamber was evacuated to a base pressure of 1×10^{-5} mbar. Titanium target (99.995% purity) of 2 in. diameter and 3.2 mm thickness was used as the source. Before depositing the films the target was sputter cleaned for 30 min (in argon) in order to remove the contamination on the target surface. Argon (15 sccm) and oxygen (4 sccm) gases were introduced inside the vacuum chamber using mass flow controllers. The source to substrate distance and the cathode power were maintained as 3 cm and 100 W respectively. And all the depositions were carried out for 15 min. The films were deposited at floating potential, −100 and −200 V bias voltages at room temperature.

2.2. Characterization techniques

The crystalline properties of the films were characterized by XRD (Bruker, D8 Focus, Germany) using CuK_α radiation in the diffraction angle range of 20–40°. The surface morphology of the films was studied by using field emission scanning electron microscope (FESEM) (Carl Zeiss SUPRA55, Germany). The elemental composition of the films was determined using energy dispersive analysis of X-ray (EDAX) attached with the FESEM. The thicknesses of the films were measured using ellipsometry (Filmmetric F20, USA) and were found to be in the range of 130–200 nm. The optical properties of the films were studied by double-beam UV–vis spectroscopy (Perkin Elmer, Lambda 35, USA) in the wavelength range of 200–800 nm.

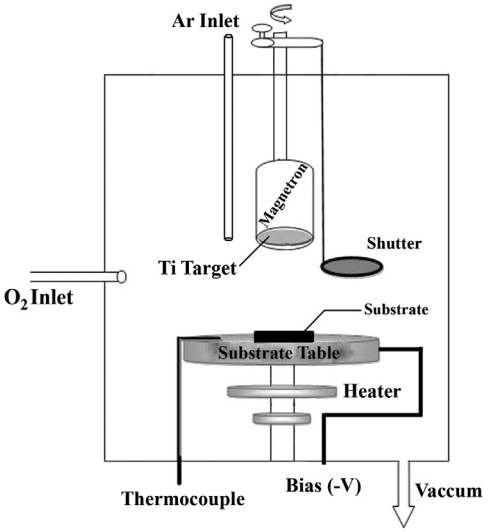

Fig. 1. Schematic representation of dc magnetron deposition setup.

2.3. Gas sensing setup

The gas sensing studies were performed in a custom built sensing setup. The schematic diagram of the gas sensing setup is shown in Fig. 2. The sensing setup consists of gas sensing chamber (volume 1 l), picoammeter (DPM-111), high voltage power supply (EHT-11) and vacuum pump (VE115N). Before injecting NH_3 inside the test chamber, the sensor with TiO_2 film as the active layer was stabilized to attain the stable baseline in ambient air. After fixing the baseline, the NH_3 was injected using a micro-syringe of required concentration. And the change in the resistance value of the TiO_2 films was constantly recorded using picoammeter.

3. Results and discussion

3.1. Structural properties

The XRD patterns of TiO_2 films deposited at floating potential, −100 and −200 V are shown in Fig. 3. The films deposited at floating potential had higher percentage of anatase phase and smaller fraction of rutile phase. The films deposited at −100 V bias consisted of smaller fraction of anatase phase and higher fraction of rutile phase of TiO_2 and with peaks corresponding to (101) and (110) planes. The films deposited at −200 V contain single phase of rutile TiO_2 with its corresponding plane at (110) and this is in concurrence with the JCPDS card no. 21-1272 [17]. The deposited film shows no other impurity peak, which suggests that the deposited films are of high purity. When increasing the bias voltage from −100 to −200 V the anatase peak (101) disappeared and large fraction of rutile phase (110) is only observed. This may be due to the fact that the anatase phase is less stable than the rutile and also substrate bias voltage increases the kinetic energy of the bombarding Ar^+ ions that creates large number of nucleation sites [18]. The crystallite size was calculated using Debye Scherrer formula [19]

$$D = k\lambda/\beta \cos\theta \quad (1)$$

where k is the shape factor, λ is the wavelength of the X-ray, β is the full-width half-maximum and θ is the diffracted angle.

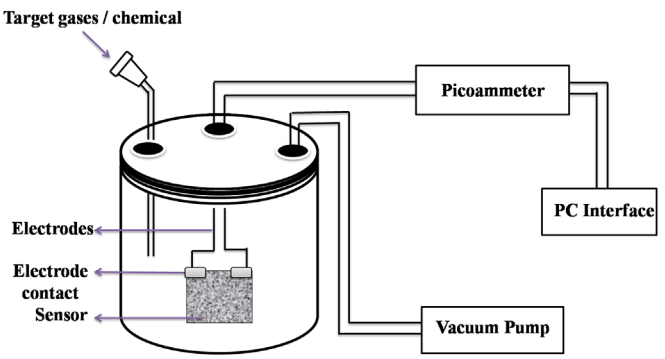

Fig. 2. Schematic diagram of gas sensing setup.