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Impedance behavior of n-type TiO_2 nanotubes porous layer in reducing vapor ambient

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ABSTRACT

Impedance behavior of n-type TiO_2 nanotubes array based vapor sensor is presented in this work with focus on the behavior of resistive and capacitive changes separately in presence of reducing organic vapors like methanol and acetone. The sensing layer of TiO_2 nanotubes array was synthesized by anodizing Ti substrate by electrochemical route. The surface morphology, crystallinity and chemical composition of TiO_2 nanotubes array were characterized with field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) spectroscopy and X-ray photoelectron spectroscopy (XPS) respectively. Gold (Au) contact was deposited on film surface by thermal evaporation technique for developing Au/TiO_2 nanotubes/Ti sensor. Cole-Cole plots of the sensor (operating at room temperature) in methanol and acetone ambient were drawn and an equivalent circuit of device was modelled to explain the sensing mechanism of the sensor.

1. Introduction

Timely detection and subsequent control of the volatile organic compounds (VOCs) is needed owing to their hazardous influence on environment, food and human health [1]. Out of many VOCs, acetone, being a bio-marker, has been widely studied in medical field [2] and a very high concentration of acetone in breath is an indicative of diabetic disease [2]. Methanol is an another popular VOC which has been widely used in fuel cells, biodiesel preparation, as a solvent in dyes, drugs, colors etc. [3]. However, methanol has toxic effects on human body and thus its timely detection is highly desirable. Sensors employing metal oxide nanostructures like ZnO, SnO_2, TiO_2 etc. are widely used for VOCs detection [4,5]. Different nanostructures used in gas/vapor sensing exhibit advantages like high surface area and lower activation energy for sensing which results in excellent sensitivity towards target gas [6].

Among metal oxides, TiO_2 is one of the most promising and stable sensing material which has been reported widely since last two decades [7]. TiO_2 has three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [8]. Rutile is the most common phase found in nature and has the lowest free energy and hence thermodynamically the most stable phase of TiO_2 [9]. Anatase occurs rare in nature but showed great interest in past as it offers the highest electron mobility among all three phases [10]. Brookite is the rarest among three and also very difficult to be synthesized [11]. Also, both anatase and brookite are metastable phases and can be transformed exothermally into rutile. TiO_2 nanostructures which were synthesized at low temperature are typically amorphous in nature. Phase transformation from anatase to rutile usually occurs around 500–700 °C [12]. However, this temperature range are dependent on various factors like particle size, strain, impurities. Anatase and rutile are the two most commonly used phases considering the application area of TiO_2 [8].

Out of many nanostructures of TiO_2, nanotubes array offers maximum free space due to the availability of its inner and outer void regions. Also, NTs grown via electrochemical anodization route readily adhere to titanium substrate which forms well oriented and perpendicularly aligned structure [13]. Thus, transport of electrons in these oriented NTs is easier than any other non-oriented nanostructures [14–16]. Hence, TiO_2 nanotubes array has the potential to be used as a sensing layer for efficient gas/vapor sensing [17–20].

Most of the reported metal oxide based sensors work in the resistive mode where sensing mechanism relies on free electron theory of chemisorption on semiconductor surface [21]. Surface reactions that take place between adsorbed oxygen molecules and the target gas/vapor result in the change of electron concentration of sensing layer and hence the resistivity [22]. Sensors can also

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work in capacitive mode in which sensing involves monitoring the change in dielectric value of the device in different ambient [24]. Though the resistive mode sensing is simple and popular from measurement aspect, capacitive sensors have gained a great interest because of its less temperature dependency that offer thermal stability and low power requirement [23].

Conventionally, planar electrode configuration is employed in sensors where two electrodes are placed on a same plane either below or above the sensing layer. However, vertical electrode configuration or metal-insulator-metal (MIM) structure can also be used in sensors where sensing layer is placed in between two electrodes. MIM structure is suitable for both resistive and capacitive mode sensing approach. Also, MIM structure is highly appropriate for one dimensional (1-D) nanostructures (like nanorod, nanotube etc.) based gas or vapor sensors where it can offer faster response/recovery at relatively low operating temperature [23].

Sensors based on metal oxide nanostructures with purely resistive [3,8,25] and purely capacitive [1,21,24] nature were reported extensively for different gases and vapors showing their efficiency in sensing performance. Y. Kwon et al. reported TiO_2 nanotube based sensor for ethanol sensing in resistive mode [25]. Z. Wang synthesized porous TiO2 for humidity sensing by monitoring impedance of sensor [5]. K. Dutta et al. fabricated Ti/TiO_2 nanotube/Ti sensors for benzene, toluene and xylene sensing in capacitive mode [21]. However, impedance analysis of TiO_2 nanotube in reducing vapor ambient is relatively less investigated. Considering the individual importance of resistive and capacitive mode sensing, current study is focused on impedance analysis technique where resistive and capacitive components of a sensing materials can be considered separately.

In the present work, TiO_2 nanotubes array was synthesized by electrochemical anodization technique and used as a sensing layer. A considerable effort was given to characterize the individual resistive and capacitive components of a sensing layer and to observe their change in presence of reducing ambient to realize the potentiality of sensing material in resistive and capacitive mode. MIM sensor device was fabricated by using Au and Ti as top and bottom electrode respectively. To identify the individual electrical parameters (resistance and capacitance) of the TiO_2 nanotubes array, device was characterized by impedance method. Impedance behavior of Au/TiO_2 nanotubes/Ti sensor towards methanol and acetone was studied by calculating real and imaginary values of impedance from Cole-Cole plot.

2. Experimental

2.1. Synthesis of TiO_2 nanotubes

TiO_2 nanotubes array was synthesized by electrochemical anodization of high purity Ti foil (99.99% purity, 0.25 mm thick) in a two-electrode configuration where anode was of Ti foil (25 mm × 25 mm) and cathode was of graphite rod (20 mm dia., 25 mm length inside the electrolyte). Schematic of anodization setup is shown in Fig. 1. Anodization was carried out at 27 °C for 90 min by applying constant DC bias voltage of 40 V through Keysight E3643A. Electrolyte is made of 0.5 wt% NH_4F, 20 vol% deionized (DI) water and ethylene glycol. The synthesis of TiO_2 nanotubes can be explained using following chemical equations:

$$Ti + 2H_2O \rightarrow TiO_2 + 4H^+ \quad (1)$$

$$TiO_2 + 6HF \rightarrow [TiF_6]^{2-} + 2H_2O + 2H^{+\cdot} \quad (2)$$

Initially, a uniform oxide layer was grown by field assisted oxidation of Ti substrate as represented in Eq. (1). Subsequently, HF

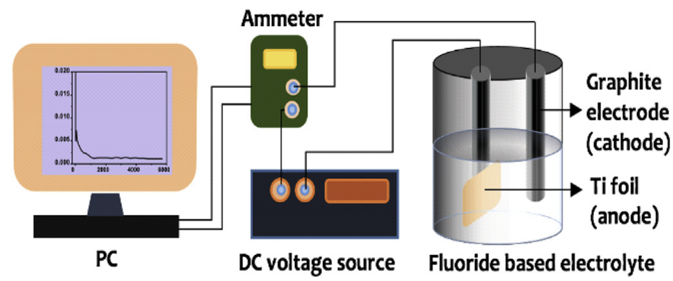

Fig. 1. Schematic of electrochemical anodization setup for the synthesis of TiO_2 nanotubes.

present in the electrolyte attacked the oxide layer and form a soluble TiF_6^{2-} complex as shown in Eq. (2). Apparently from Eq. (2), oxide layer started to etch and pores were created in oxide layer. Simultaneous oxidation and etching were responsible for the formation of nanotubes. After anodization, grown nanotubes sample was washed in DI water. After drying, TiO_2 nanotubes/Ti sample was annealed at 330 °C for 3 h in a closed annealing furnace for enhancing its mechanical strength [23]. In sensing application, gas sensor need to be stable in terms of its resistance and capacitive values. As synthesized TiO_2 NTs are seldom used in gas sensing because of its unstable nature. Annealing is required in this experiment to increase the crystallinity and mechanical strength of TiO_2 NTs. An optimum annealing temperature of 330 °C was used so that anatase phase should not convert into rutile phase.

2.2. Characterizations

TiO_2 nanotubes/Ti sample was characterized by X-Ray Diffraction (XRD, Model: D/max-RAPID Rigaku micro-diffractometer) to determine composition and phase of crystallinity. Field Emission Scanning Electron Microscopy (FESEM, Model: Nova Nano FE-SEM 450) was employed to determine the morphological parameters like tube length, diameter, wall thickness and pore size of the nanotubes array. Chemical composition of TiO_2 nanotubes array was investigated using X-ray photoelectron spectroscopy (XPS, VSW CLASS 150, monochromatic Mg-Kα source).

2.3. Device fabrication and impedance measurement

Schematic of the fabricated device is represented in Fig. 2. Sensor employing two vertical electrodes separated by a dielectric medium was fabricated to get a Metal- Insulator- Metal (MIM) type structure. For top electrode contact, Au film (1 mm × 1 mm × 100 nm) was deposited over TiO_2 nanotubes/Ti sample (2 mm × 7 mm) by thermal evaporation technique. Ti substrate was used as the bottom electrode contact. TiO_2 nanotubes array was used as the dielectric medium (and sensing layer also) between two electrodes.

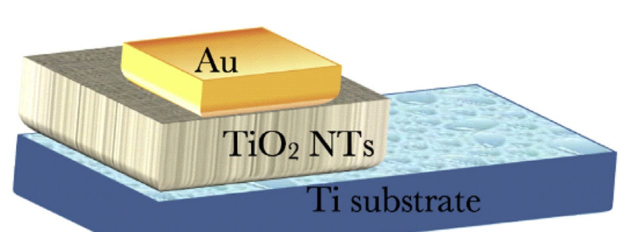

Fig. 2. Schematic of MIM structure based device.