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Investigation of RF sputtered tungsten trioxide nanorod thin film gas sensors prepared with a glancing angle deposition method toward reductive and oxidative analytes

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ABSTRACT

The gas-sensing performances of tungsten trioxide nanorod thin-films toward reducing and oxidizing analytes are reported. The nanostructured thin-films were RF sputtered, via a glancing angle deposition (GLAD) technique, with different thickness onto conductometric transducers. Thin-film microcharacterization of the surface morphology, chemical compositions and crystal structure by SEM, TEM, XRD and XPS showed that the thin layers contained highly porous, nanocrystalline, stoichiometric WO_3 nanorod features with average height varying from 140 to 420 nm and diameter ranging from 40 to 60 nm. Initial vapor sensing test results showed that the ethanol response of WO_3 nanorod thin-film tended to increase with decreasing film thickness. The optimized sensor operating temperature for ethanol detection was 300 °C with a maximum response of 10 to C_2H_5OH of 200 ppm for the thinnest film. In contrast, the NO_2 response was improved by increasing the WO_3 nanorod film thickness, and the thickest films exhibited a very large response of 1075 (10 ppm of NO_2) at a relatively low optimized operating temperature of 150 °C. Moreover, the developed WO_3 based sensors showed good repeatability characteristics when exposed to C_2H_5OH, but exhibited some poisoning effects when tested in an NO_2 environment. The interesting surface structure with very high surface-to-volume ratio of the thin films was reasoned to be responsible for the high and fast response when exposed toward both analytes.

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1. Introduction

Nanostructured based metal oxide thin films have been of great interest in the applications of gas sensing due to their huge surface-to-volume ratio and high density of surface sites [1,2]. These thin-film sensors operate based on a change of the surface conductivity of the active material due to surface chemical adsorption of gas species and related space charge effects [3,4]. High quality nanostructures are key to achieving highly responsive sensing devices. Features that improve the quality of nanostructured thin-films include, but are not limited to, size and spacing of nanostructures and their crystallinity. Nanostructures with high porosity are known to possess high surface-to-volume ratios, leading to the enhanced reaction rates between the surface and the molecules [5]. As a result, their gas detection capability increases dramatically with a decrease in structural dimensions and grain size [6]. A number of deposition methods have been employed to obtain various novel metal oxide nanostructures for a myriad for applications ranging from land to space [7]. Single nanowires and its array based devices have been demonstrated to offer great potential in achieving high sensitivity due to their ultrahigh surface-to-volume ratio [5,6]. However, the control of single nanostructure formation has been a significant challenge, and this novelty is still in the early stages of exploration. Presently, a single nanostructure device still requires expensive micro- or nano-scale fabrication processes, such as e-beam lithography and nano-manipulation, which are impractical for commercial applications. Thin-films comprising of nanostructures are practical alternatives that also offer high sensing performances.

Nanostructures such as nanorods, nanowires, and nanofibers based on tungsten trioxide (WO_3) thin-films have been widely investigated due to its various unique properties [8–10]. Numerous experiments have been reported in regards to its applications, such as in gas sensing and solar cells [11–13]. This n-type semiconductor

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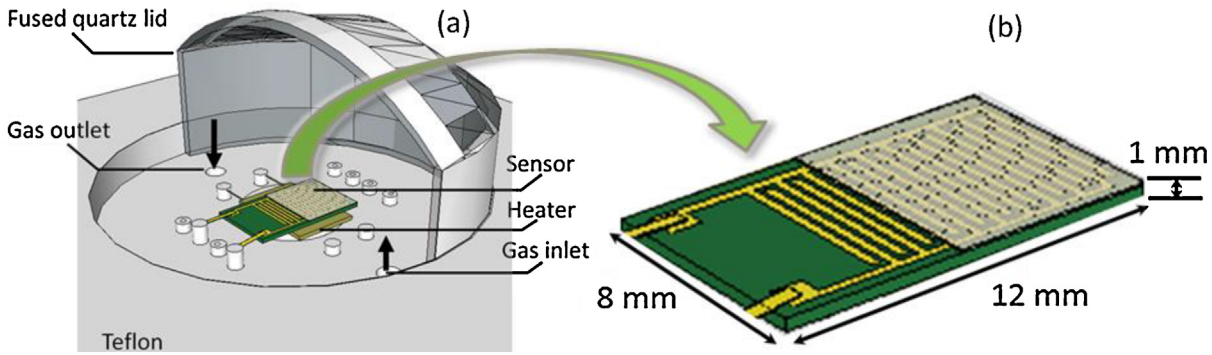

Fig. 1. (a) Schematic of the custom-built gas chamber (b) author's illustration of the fabricated sensor with WO_3 thin film.

is known to be very sensitive toward reducing and oxidizing gas such as ethanol [8,14] and NO_2 [10,15–17]. Ethanol is a common volatile organic compound (VOC) widely used in many commercial applications, such as drinks, food, and fuel for vehicles. However, drunk driving often causes fatal road accidents, thus alcohol in driver's breath is controlled by law in many countries so as to not exceed 150–200 ppm. Thus, Ethanol detection is of high interest, and WO_3 based sensors are potential candidates. Furthermore, NO_2 is a highly toxic gas that can cause acute respiratory illness in children when exposed at a concentrations greater than 53 ppb [6]. The excellent response toward NO_x gases makes WO_3 based sensors relevant for commercial applications, which focuses on monitoring toxic gases as well as detecting leakage/pollution in the industrial and automotive applications [15,18].

WO_3 nanostructures can be prepared by a number of methods including thermal oxidization, flame spray pyrolysis, chemical vapor deposition, physical vapor deposition, e-beam lithography, nanolithography, and template-growth techniques [19–23]. However, these methods are either expensive and complicated or unreliable due to poor control of nanostructure formation; consequently, they are unsuitable for commercial applications. Recently, glancing angle deposition (GLAD) based on DC sputtering process has been developed to produce well-ordered WO_3 nanorods on alumina substrates for NO_2-sensing applications [24].

Here, we study GLAD-RF-sputtered WO_3 nanorod thin-film gas sensors prepared with different controlled thicknesses on SiO_2/Si substrates for C_2H_5OH and NO_2 sensing applications. The developed nanostructured WO_3 based sensors were tested at operating temperatures ranging from 100 °C to 450 °C for C_2H_5OH and NO_2 in concentrations in the range of 10–200 ppm and 0.5–10 ppm, respectively. The sensing performances toward C_2H_5OH and NO_2 will be described herein.

2. Experimental methods

2.1. WO_3 film deposition

WO_3 based gas sensors were fabricated by RF sputtering with the GLAD technique. The WO_3 nanostructured films were sputtered onto pre-fabricated interdigitated (IDT) electrodes made of SiO_2/Si based substrates. Thin layers of SiO_2 (~300 nm), Cr (~50 nm) and Au (~100 nm) were successively electron-beam evaporated onto the Si substrates. Once these steps were completed, a standard photolithographic patterning process was applied to obtain the IDT. The Au/Cr IDTs contained 8 finger pairs with spacing of 50 μm (Fig. 1(b)). Prior to WO_3 deposition, the fabricated transducers were cleaned successively with acetone and isopropanol under ultrasonication and dried in a flow of nitrogen (N_2). Once ready, the samples were attached on a substrate holder and loaded into the deposition chamber.

WO_3 nanorods were deposited in a variable angle RF magnetron sputtering system. The sputtering target was a 3-inch tungsten disc with 99.995% purity (K.J. Lesker). The distance from the target to substrate center and the substrate rotation were set at 7 cm and 30 rpm, respectively [19]. The substrate normal was positioned at an angle of 85° with the respect to the vapor incident flux (the vertical axis). The chamber was evacuated by rotary and turbo molecular pumps (Pfeiffer Inc.), while the vacuum pressure was continuously monitored with Pirani and Penning pressure gauges to a base pressure of 5.6×10^{-6} mbar. The tungsten target was then reactively sputtered in a mixture of 99.999% argon (Ar) and 99.999% oxygen (O_2) at controlled flow rates of 9.6 and 11.0 sccm, respectively. The plasma discharge was generated at a constant RF power of 200 W at a sputtering pressure of 5.0×10^{-3} mbar. The film thicknesses were varied by changing sputtering time from ½ to 2 h. The samples deposited at ½, 1, and 2 h were labeled as W1, W2 and W3, respectively. The fabricated samples containing tungsten oxide based thin-films were then annealed in air at 450 °C for 2 h with a ramp up/down of 2 °C/min.

2.2. Micro-characterization techniques

The crystal structures of the WO_3 nanorods were confirmed by grazing-incidence X-ray diffraction (GIXRD, Rigaku Ttrax III). The Cu-Kα radiation was operated at 50 kV, 300 mA with a scanning speed of 2° per minute at a 2θ step of 0.02°. The morphology and film thickness of the WO_3 nanorods were examined by field-emission scanning electron microscopes (FE-SEM, Hitachi S-4700 and FEI Nova NanoSEM). X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific K-Alpha photoelectron spectrometer equipped with monochromatic Cu Kα radiation and 400 μm spot size. Surveys and peaks were scanned at 200 and 50 eV pass energy, respectively. During the analysis, a flood gun was used to minimize charging effects. Transmission electron microscopic (TEM, JEOL 2010) as well as selected area electron diffraction (SAED) images were obtained at 200 kV. The TEM specimen was prepared via drop casting several droplets of the mixture (scratched thin-film layers suspended in ethanol) onto an amorphous carbon coated copper grid and allowed to dry in air.

2.3. Experimental setup for C_2H_5OH and NO_2 sensing test

Nitrogen dioxide (NO_2) as an oxidizing agent and ethanol (C_2H_5OH) as the reducing agent were used to investigate the sensing performances of the developed nanostructured WO_3 sensors. The sensors were exposed to controlled concentrations of analyte, which was flowed into the gas-sensing chamber setup via the mass flow controllers (MFCs). The gas-sensing chamber is connected to an external power supply used to control the heater underneath the sensor (Fig. 1(a)). A thermocouple was placed on

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