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On the influence of temperature gradient of annealing process on the nano-structure and sensing properties of WO_3 thin films to NO_2 gas and relative humidity

K. Khojier [a,*], H. Savaloni [b], N. Habashi [a], M.H. Sadi [a]

[a] Department of Physics, Faculty of Science, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[b] Department of Physics, University of Tehran, North Kargar Street, Tehran, Iran

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ABSTRACT

This research presents a detailed study of the influence of temperature gradient of the annealing process on nanostructure, porosity and the sensitivity of sputtered WO_3 thin films to NO_2 gas and relative humidity that can be used for the development of metal oxide gas sensors. WO_3 thin films were deposited by DC reactive sputtering method and then post-annealed in the air at 500 °C with different temperature gradients (gradual, step by step and rapid annealing). Morphological and structural investigations were carried out on all samples by atomic force microscopy and X-ray diffraction method. Porosity and effective surface area were measured by physical adsorption isotherm. Electrical response of all prepared films was tested to 10 ppm NO_2 gas at the operating temperature range of 50–250 °C and humidity at room temperature. Results showed that gradually annealed sample had the best sensitivity to NO_2 gas and the relative humidity due to the most effective surface area.

1. Introduction

The detection of nitrogen oxides (NO_x) is crucial for monitoring environmental pollution resulting from combustion processes, particularly industrial emissions or vehicle exhaust [1]. In the case of air-quality system, NO_2 being the main gas to be detected, mainly because NO in ambient atmosphere, easily oxidizes to NO_2 [2]. Furthermore, NO_2 gas is the main precursor for ozone layer depletion in lower atmosphere and also produces acid rain which is slowly damaging the ecosystem [3,4]. Among the various transition metal oxides, undopped and dopped WO_3 in the form of thick and thin films have been reported to have remarkable ability for the detection of toxic and flammable gases such as NO_x [4–10], H_2S [11,12], NH_3 [7,10,13], CO [14], H_2 [5,9,15,16] and LPG [10]. WO_3 is an n-type semiconductor and shows a resistance increase in the presence of NO_2 gas (an oxidizing gas) [17].

Sensitivity of metal oxide semiconductor gas sensors is strongly affected by micro-structural factors such as grain size or grain boundary [18], film thickness [19–21], density [21], porosity and effective surface area [5,22,23], crystallinity [23], and dopants [12,14,20]. Among these factors, it seems that porosity and surface area play special roles, because the target gas interacts with the surface of the metal oxide film (generally through surface adsorbed oxygen ions) and results in a change in the charge carrier concentration of the material. Therefore, enhancing the contact surface with the target gas is an important factor in improving the sensitivity, and this can be obtained by increasing the porosity and effective surface area of the sensor. Prior, the effect of porosity or effective surface area on sensitivity of the above mentioned sensors have been studied by many researchers. They have used various methods and parameters for obtaining the pores structure. Shen et al. [5] investigated the sensing properties of DC reactive sputtered WO_3 thin films for H_2 and NO_2 gases. They studied the effect of discharge gas pressure on pore size and effective surface area and subsequently sensing properties. Li et al. [22] studied the effect of surface area on sensitivity of SnO_2 thin films which synthesized by the surfactant method for H_2 and CO gases. Liu et al. [23] prepared WO_3 thin films by post-annealing of DC reactive sputtered tungsten oxide thin films and investigated the annealing temperature effect (in the range of 200–650 °C) on porosity and sensitivity to NO_2 gas. Furthermore, in our earlier work [24] we showed that the sensitivity of MoO_3 thin films deposited using the DC reactive sputtering method with different argon gas flows to CO gas improves by increasing the surface roughness as a result of increased effective surface area.

Liu et al. [23] obtained the highest sensitivity of the DC reactive sputtered WO_3 thin films to NO_2 gas at the annealing temperature of 500 °C while it decreased at 650 °C as a result of formation of

* Corresponding author. Fax: +98 21 88561406.
E-mail addresses: khojier@iauc.ac.ir, k_khojier@yahoo.com (K. Khojier).

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microcracks in the films structure. Therfore, it may be deduced that annealing temperature of 500 °C should be the most suitable temperature for production of WO_3 thin films for use in the gas sensing devices. Considering this result, the aim of this work is to investigate the influence of temperature gradient of annealing process for final temperature of 500 °C on the nano-structure, surface morphology, porosity, effective surface area and the sensitivity of WO_3 thin films to NO_2 gas and humidity.

2. Experimental details

2.1. Thin films preparation

Ultrasonically cleaned n-type Si(400) substrates were oxidized in a horizontal tube furnace (Exciton, 1200-30/6, T.H, Iran equipped to Shinko temperature programmable controller – PCD 33A) with an oxygen gas flow of 200 standard cubic centimeter per second (sccm) at 1100 °C to obtain SiO_2 layer. In order to fabricate gas sensing elements based on WO_3 thin films, a pair of Pt interdigital electrodes with gaps of 50 μm and thickness of 50 nm was first formed on the SiO_2/Si (400) substrates. The device was then annealed at 500 °C for 90 min with flow of (200 sccm) high purity argon gas in the above mentioned furnace. WO_3 thin films of 90 nm thickness were deposited on Pt/SiO_2/Si substrates by a DC reactive magnetron sputtering system using high purity circular W target (99.98%) of 76 mm diameter and 1 mm thickness at room temperature. The target to substrate distance was 10 cm. A continuously variable DC power supply of 700 V and 120 mA was used as a power source for sputtering. The thickness and the deposition rate of these tungsten oxide films were checked in situ using a quartz crystal monitor (6 MHzgold, Inficon Company, USA) positioned close to the substrate during the sputtering process. The deposition rate for all deposited films was 4 Å/s. The sputtering chamber was pumped down to 1×10^{-6} mbar using a turbo molecular pump prior to introduction of an Ar/O_2 gas mixture. The ratio of Ar/O_2 was 1:1 during deposition process and the flow rates of argon and oxygen gases were controlled individually by mass flow controllers. Post-annealing of prepared tungsten oxide thin films was also performed in the above mentioned furnace in the air environment at 500 °C with different gradients of annealing temperature including gradual annealing (sample I), step by step annealing (sample II), and rapid annealing (sample III). Detailed information of this process is shown in Fig. 1.

2.2. Thin films characterization

Crystallographic structure of the produced films was obtained using a Philips XRD X'pert MPD Diffractometer (Cu K_α radiation) with a step size of 0.02° and step time of 1 s. An atomic force microscope (AFM) (Auto probe PC, Park Scientific Instrument, USA) was also used for investigation of the surface morphology and roughness of the samples.

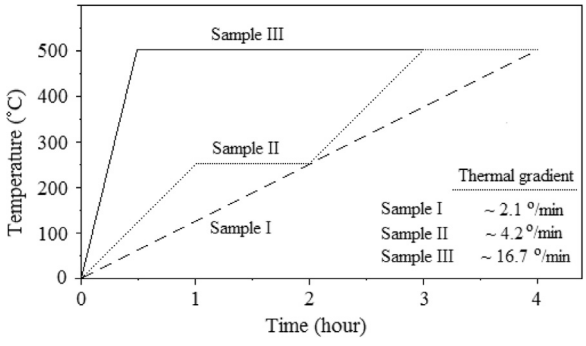

Fig. 1. Processes of annealing of three WO_3 samples using different temperature gradients.

The pore size distribution and effective surface area of the films were determined by a Quantachrome AUTOSORB-1-MP at liquid nitrogen temperature. For pore size distribution determination, isothermal adsorption–desorption of Ar gas was carried out. The effective surface area of WO_3 thin films was also obtained by isothermal Kr gas physical adsorption measurements.

In order to investigate the gas sensing of the samples, they were positioned on a hot plate inside an airtight stainless steel chamber. A DC power supply was used to supply the current to the heat elements of the hot plate. The operation temperature of the sensor was measured by a thermocouple mounted on the substrate. The current–voltage measurements were carried out on the samples at different DC voltages and the change in the current with time was recorded. The electrical response of the films was tested to 10 ppm NO_2 gas at different temperatures in the range of 50–250 °C. The electrical response, response time and recovery time were measured in this test in order to investigate the sensitivity of the samples. The gas response is defined as $S=(R_g-R_a)/R_a$, where R_g and R_a are the electric resistance of a sensitive film in a measuring gas and that in clean air, respectively. The response time is the time interval over which resistance of the sensor materials attains a fixed percentage (usually 90%) of final value when the sensor is exposed to full scale concentration of the gas. The recovery time is also the time interval over which resistance reduces to 10% of the saturation value when target gas is switched off and the sensor is placed in synthetic air.

The humidity response measurement was also carried out in a climate chamber at ambient temperature in the relative humidity range from 10% to 90%. The chamber had a relative humidity range of 10–95%. The deviation of the relative humidity during measurement was 3%, and to avoid experimental error, the time was lingered for 10 min at each measuring point.

3. Results and discussion

3.1. Crystallographic structure and surface morphology

As reported in Ref. [25], several allotropic modifications exist for WO_3, such as monoclinic, orthorhombic and tetragonal. These crystalline structures are strongly affected by temperature, impurity and substrate material [3,25]. Table 1 lists some references which used the sputtering deposition technique and subsequently post-annealing method to prepare the WO_3 thin films, similar to our work, and reported monoclinic structure for WO_3 thin films. These references show that the monoclinic is a favorite crystalline structure for WO_3 thin films which deposited by sputtering technique on the oxidized Si substrate and then annealed at temperature range of 350–600 °C.

Fig. 2 depicts X-ray diffraction patterns of tungsten oxide thin films annealed at 500 °C with different temperature gradients of annealing process. XRD patterns of all samples show three diffraction lines which can be attributed to the crystallographic orientations of (200), (202), and (400) of WO_3 with monoclinic structure (with reference to JCPDS Card No. 83-0950, 2Θ: 24.3668°, 34.1673°, and 49.9325°; space group: P21/n). As can be seen in Fig. 2, the WO_3(200) diffraction line dominates other mentioned diffraction lines, so that it can be assumed as a preferred orientation of these samples. In order to quantify the degree of preferred orientation in the samples produced in this work the XRD patterns of all samples were examined and the preferred orientation of the samples was evaluated from [27]: