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Low temperature CO sensitive nanostructured WO_3 thin films doped with Fe

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ABSTRACT

Nanostructured tungsten oxide thin film based gas sensors have been developed by thermal evaporation method to detect CO at low operating temperatures. The influence of Fe-doping and annealing heat treatment on microstructural and gas sensing properties of these films have been investigated. Fe was incorporated in WO_3 film by co-evaporation and annealing was performed at 400 °C for 2 h in air. AFM analysis revealed a grain size of about 10–15 nm in all the films. GIXRD analysis showed that as-deposited films are amorphous and annealing at 400 °C improved the crystallinity. Raman and XRD analysis indicated that Fe is incorporated in the WO_3 matrix as a substitutional impurity, resulting in shorter O—W—O bonds and lattice cell parameters. Doping with Fe contributed significantly toward CO sensing performance of WO_3 thin films. A good response to various concentrations (10–1000 ppm) of CO has been achieved with 400 °C annealed Fe-doped WO_3 film at a low operating temperature of 150 °C.

1. Introduction

Tungsten oxide (WO_3) is an n-type wide band gap metal oxide semiconductor. Like other metal oxides such as SnO_2, TiO_2, In_2O_3 and ZnO, WO_3 has become a promising material for gas sensing devices due to its inherent electrical conductivity and excellent sensitivity and selectivity toward various gases such as NO_2 [1], NH_3 [2], H_2S [3], O_3 [4], H_2 [5] and Volatile Organic Compounds (VOC) [6]. However, as for any other metal oxide based gas sensor, they operate efficiently only in the temperature range 200–500 °C [7]. Low fabrication costs combined with low power consumption and a promise of high gas sensitivity toward specific gases are the driving force behind research on WO_3 for improved gas sensing properties. Deposition techniques of WO_3 films vary from acidic precipitation [8], RF sputtering [9], magnetron sputtering [10,11], hard template route [12], pulsed laser deposition [13], solgel [6] and thermal evaporation [14,15]. The gas sensing mechanism is based on bulk resistance changes of the WO_3 film induced by reactions between the target gases and the film surface. In air environment, oxygen molecules adsorb onto the surface of metal oxide layer to form O_2^-, O^- and O^{2-} species by extracting electrons from the conduction band depending on the temperature [16] and type of metal oxide (n-type or p-type). For n-type sensor material like WO_3 and a reducing gas, the gas reacts with oxygen ions to form neutral molecules, leading to electron transfer to the sensor material and a resulting decrease in resistance. The microstructural properties of the film have a significant impact on sensing performance. The grain size, film thickness, porosity and heat treatment control the sensor performance. Film thickness can have significant effect in optimizing sensor selectivity and sensitivity [17]. Nanosized materials have a very large surface area which offers more surface/gas interaction thereby enhancing the sensing properties. Sensing measurements on nanostructured WO_3 deposited by thermal evaporation have shown promising performances toward sub-ppm concentrations of NO_2 [14]. Mesoporous nanostructured WO_3 films have shown a high sensitivity to NO_2 even at low concentrations [12]. WO_3 thin films with smaller grain size obtained by rf sputtering have shown enhanced sensitivity to oxidizing gases [18]. Annealing of WO_3 films after deposition has been reported to improve crystallinity and well defined grain boundaries in the film [11,19,20]. The addition of metals or metal oxides to WO_3 film can also enhance the sensor performance. Tungsten oxide co-loaded with TiO_2 shows an enhanced sensing performance to NO and NO_2 [21]. Microstructural analysis of co-evaporated films of TiO_2 and WO_3 powders revealed nanoporous films with enhanced porosity [15]. The sensing performance for NO_2, O_3 and C_2H_5OH is also enhanced using mixed tungsten and iron oxide thin films [9]. Addition of La_2O_3 to WO_3 nanoparticles improved the response toward VOC and the highest gas response shifted toward low temperature [6]. Improved response toward NO_2 by introducing Cu as a catalytic additive in

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WO_3 films has also been reported. This was mainly attributed to copper segregating at the material surface as Cu(I) [12]. However, there is little evidence indicating response of WO_3 thin films toward CO in the literature [22].

Inclusion of noble metal impurities such as Au, Ag, Pd or metal oxides such as TiO_2 in WO_3 thin films have shown an improved sensitivity toward various gases, which is mainly attributed to the noble metal catalytic effect on the gas/surface interaction [23,24]. However, gas sensing properties of iron-doped WO_3 thin films have not been well documented. In this paper, iron has been used to dope the WO_3 thin films. Since iron has a similar atomic radius (0.64 nm) as W (0.62 nm), it can be introduced as a substitutional impurity in the WO_3 crystal structure to produce crystal distortions, and its influence on physical, chemical, electronic and gas sensing properties can be investigated. Recently, the addition of Fe to electron beam evaporated (EBE) films has been shown to improve sensitivity toward NO_2 and acetaldehyde at 200 °C [25,26]. In this paper, we present the CO sensing performance of iron-doped thermally evaporated WO_3 thin films at a lower operating temperature of 150 °C and discuss this from a microstructural point of view.

2. Experimental

2.1. Sample preparation

Thermal evaporation was used to deposit thin films of tungsten oxide and iron-doped tungsten oxide (0.5 at% Fe). WO_3 thin films were deposited on silicon substrates with interdigitated Pt electrodes (Electronics Design Center, Case Western Reserve University, Cleveland, USA). The size of the substrate was 8 mm × 8 mm × 0.5 mm. The electrode fingers have a line width and height of 100 μm and 300 nm, respectively. Powders of tungsten oxide (99.9% purity, grain size 20 μm) and iron (99.9% purity, grain size 100 μm) from Sigma Aldrich Pty Ltd., were used as evaporation sources. Before the deposition, the powders were placed in desiccator to avoid any moisture and decontamination. For the purpose of doping, iron was mixed thoroughly with WO_3 and the mixture was evaporated.

A bell jar type PVD unit (Varian Coater with AVT Control System, Australia) was used to deposit the WO_3 thin films. The substrates were mounted on a substrate holder which was placed at a distance of 38 cm in line of sight from the evaporation source. Deposition was carried out at 4×10^{-5} mbar. Powder was deposited onto the substrates at a rate of 35 nm s^{-1}. A quartz crystal film thickness monitor was used to control the thickness of films. The film thickness was restricted to 300 nm and the effect of grain size, porosity, crystallinity and heat treatment for a given film thickness has been investigated. After the deposition, the films were annealed at 400 °C for 2 h in air to improve the microstructural properties and relieve any thermal stresses in the films.

2.2. Sample characterization

A JEOL 1200 TEM was used at an accelerating voltage of 120 kV to investigate the size and shape of WO_3 nanoparticles, crystalline structure and distribution of dopant in the film. An NT-MDT P47 Solver Scanning Probe Microscope was used to study the surface morphology of the films. The WO_3 film surface was scanned by a silicon tip (radius of curvature 10 nm) in semi-contact mode over an area ranging from 0.25 μm^2 to 4 μm^2. The mean grain size and grain distribution and surface roughness were determined using the Nova NT-MDT Image Analysis Software. The concentration profile of constituent elements in WO_3 film was determined using RBS analysis. RBS measurements were carried out with a 1.8 MeV He^+ beam under a vacuum of 7×10^{-6} mbar. XPS analysis was performed using Kratos AXIS Ultra XPS incorporating a 165 mm hemispherical electron energy analyzer, and using monochromatic Al K_α X-rays (1486.6 eV) at 150 W (15 kV, 10 mA), incident at 45° to the sample surface. Photoelectron data was collected at take off angle of 90°. Survey (wide) scans were taken at analyzer pass energy of 160 eV and multiplex (narrow) high resolution scans at 20 eV. Survey scans were carried out over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0×10^{-9} mbar and during sample analysis 1.0×10^{-8} mbar. Depth profiling of the film was also carried out by etching the surface with Ar source at a rate of 10 nm s^{-1}. GIXRD analysis was performed on PANanalytical XPert Pro Multi Purpose Diffractometer (MPD). A Cu K_α radiation of wavelength 1.540 Å was used. The incident angle was kept at 2° and the 2θ range was kept between 10° to 85° with a step size of 0.05°. Raman measurements were performed using an Oceanoptics QE 6500 spectrometer. A 532 nm line from an argon ion laser was used as the excitation source. To avoid local heating of the samples, small power of about 5 mW was used on the samples. A Raman shift between wavenumbers 200 cm^{-1} and 1200 cm^{-1} has been measured. The WO_3 sensor responses to various concentrations (10–1000 ppm) of CO at various operating temperatures (100–300 °C) were measured. CO was diluted in synthetic air to achieve the desired concentrations. For all the experiments, the total flow was adjusted to 200 sccm. The response of the films to reducing gases such as CO denoted as $S_{reducing}$ is defined as the ratio:

$$S_{reducing} = \frac{R_{air} - R_{gas}}{R_{gas}} \quad (1)$$

where R_{air} is the resistance in air under stationary conditions and R_{gas} represents the resistance after the sensor is exposed to the target gas during a definite time. Eq. (1) can be applied for n-type material such as WO_3 and reducing gas such as CO.

The response curve was recorded under a continuous flow of known amount of CO. A sequence control computer was utilized to computerize the pulse sequence of the CO concentrations. Initially, synthetic air was passed through the chamber at testing temperature until the stable baseline resistance was observed. Then a sequence of target gas pulse was generated for 10 min followed by synthetic air pulse. This procedure was continued until a stable baseline was observed after alternate pulses. This was followed by the experimental sequence of pulses and data was recorded. Each sensor was tested at temperatures between 100 °C and 300 °C at intervals of 50 °C under various concentrations of CO, and optimum operating temperature was determined. This was followed by two full range tests for each sensor and CO at the optimum operating temperature.

3. Results and discussion

The as-deposited as well as 400 °C annealed WO_3 films did not show any response to CO in the temperature range 100–300 °C. However, after doping with Fe and subsequent annealing, a maximum response toward CO was observed at an operating temperature of 150 °C. Fig. 1 shows the dynamic resistance curve and response of 400 °C annealed Fe-doped WO_3 film upon exposure to CO.

The film shows a stable response curve with a maximum response of $S = 20\%$ and a small response time of 64 s to 1000 ppm CO. The dominant species on the film surface at 150 °C is O_2^- [27]. The conduction mechanism is governed by the following equation [28].

$$2CO + O_2^- \rightarrow 2CO_2 + e^- \quad (2)$$