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Thin film deposition and characterization of pure and iron-doped electron-beam evaporated tungsten oxide for gas sensors

Tuquabo Tesfamichael [a,*], Masashi Arita [b], Thor Bostrom [c], John Bell [d]

[a] Faculty of Built Environment and Engineering, School of Engineering Systems, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia
[b] Graduate School of Information Science and Technology, Hokkaido University, Kita-14, Nishi-9, Kita-ku, Sapporo, 060-0814, Japan
[c] Faculty of Science and Technology, School of Physical and Chemical Sciences, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia
[d] Centre for Built Environment and Engineering Research, Queensland University of Technology, 2 George Street, Brisbane, QLD 4000, Australia

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ABSTRACT

Pure tungsten oxide (WO_3) and iron-doped (10 at.%) tungsten oxide (WO_3:Fe) nanostructured thin films were prepared using a dual crucible Electron Beam Evaporation (EBE) technique. The films were deposited at room temperature under high vacuum onto glass as well as alumina substrates and post-heat treated at 300 °C for 1 h. Using Raman spectroscopy the as-deposited WO_3 and WO_3:Fe films were found to be amorphous, however their crystallinity increased after annealing. The estimated surface roughness of the films was similar (of the order of 3 nm) to that determined using Atomic Force Microscopy (AFM). As observed by AFM, the WO_3:Fe film appeared to have a more compact surface as compared to the more porous WO_3 film. X-ray photoelectron spectroscopy analysis showed that the elemental stoichiometry of the tungsten oxide films was consistent with WO_3. A slight difference in optical band gap energies was found between the as-deposited WO_3 (3.22 eV) and WO_3:Fe (3.12 eV) films. The differences in the band gap energies of the annealed films were significantly higher, having values of 3.12 eV and 2.61 eV for the WO_3 and WO_3:Fe films respectively. The heat treated films were investigated for gas sensing applications using noise spectroscopy. It was found that doping of Fe to WO_3 produced gas selectivity but a reduced gas sensitivity as compared to the WO_3 sensor.

1. Introduction

Various techniques have been used to deposit metal oxide thin films for gas sensing applications. This includes sol–gel, chemical vapor deposition, advanced gas deposition, and physical vapor deposition [1–6]. Each of the film deposition techniques has its own advantages and limitations. The gas sensing properties of the metal oxides are determined by their intrinsic properties, but can also be enhanced by adding impurities, reducing particle size, and modifying the surface morphology and porosity of the films. Thin films are usually compact and the sensing layer is limited to the surface, whereas thicker films are commonly porous and hence the whole layer can interact with the gas species. If a controlled porosity can be achieved, then the gas sensing properties of nanostructured thin films can be enhanced significantly [7]. A theoretical study has shown that the sensitivity for gas detection can be improved if the grain size is smaller than 50 nm [8]. Film thickness can have a significant effect in optimizing sensor selectivity and sensitivity [9]. Gas detecting sensitivity also depends on the reactivity of the film surface as sensors are strongly influenced by the presence of oxidizing or reducing gases on the surface. Film reactivity and adsorption of gas species can be enhanced by adding impurities, incorporating defects and active species on the surface of the films. It has been shown that inclusion of different doping metals in the oxide films has increased the sensitivity to specific gases [10–16]. Gas detection capacity can also be enhanced by mixing metal oxides since each material has its own response and the mixture can add sensitivity and selectivity to specific gas species and also often improves sensor quality and performance [7,17–19]. It has been reported that an increased response towards certain gases was observed when iron oxide was added to the tungsten oxide film [20]. Therefore an aim of this paper is to investigate the effect of iron doping on the gas sensing properties, as well as to characterize the pure and iron-doped tungsten oxide films in order to determine the microstructure of the films and their composition, crystallinity and optical properties. In addition, gas sensing measurements of the pure and iron-doped tungsten oxide films have been performed and some preliminary results are reported in this paper.

In this paper an Electron Beam Evaporation (EBE) process has been used to produce pure and iron-doped tungsten oxide thin films. Deposition of tungsten oxide using EBE can produce a nanostructured thin film with a porosity suitable for gas sensing applications. However

* Corresponding author. Tel.: +61 731381988; fax: +61 731381516.
E-mail address: t.tesfamichael@qut.edu.au (T. Tesfamichael).

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the properties of iron-doped tungsten oxide films prepared by EBE for these applications are not well documented in the literature and this paper presents an investigation into these properties Atomic Force Microscopy (AFM) was used to study the surface morphology of the films. The chemical composition was investigated using X-ray photoelectron spectroscopy (XPS), and the crystalline nature of the films was determined using Raman spectroscopy. The optical properties of the films have been characterized using UV–Vis–NIR spectroscopy.

Table 1
Average particle diameter and average surface roughness of the WO_3 and WO_3:Fe films calculated from AFM contact mode scans using Nova image analysis software.

Material	Particle diameter (nm)	Surface roughness (nm)
WO_3	–	2.4
WO_3 (annealed)	9	2.6
WO_3:Fe	12	3.2
WO_3:Fe (annealed)	12	2.9

2. Experimental methods

2.1. Sample preparation

Pure tungsten oxide and iron-incorporated tungsten oxide thin films (10 at.% Fe) were produced using the EBE technique. The deposition of the films was performed simultaneously on both glass and alumina substrates. The glass substrate used was microscopy glass slides (Manufacturer: Matsunami Glass Ind. Ltd., Japan; Production Number: S1111) and was used for characterization of the films. Polycrystalline alumina substrate was used for manufacturing of the sensors. The dimensions of the substrates were 12 mm × 12 mm (glass) and 8 mm × 8 mm (alumina). The alumina substrate had a pre-printed gold-electrode on the film (front) side and a pre-printed platinum heating-element on the back side. The gold-electrodes were separated by a distance of 0.3 mm. Prior to film deposition the glass substrate was well cleaned with acetone.

A 10 mm diameter WO_3 pellet (99.9% purity) and 99.95% purity Fe were used as source targets for evaporation. The WO_3 was first baked in an oven at 800 °C for 1 h in vacuum before being used for evaporation to remove any moisture in the material. The electron beam evaporator has dual electron-guns that allow the simultaneous co-evaporation of two materials. The WO_3 and Fe targets were placed separately in two copper crucibles that were kept in the water-cooled copper hearth of the two electron guns for evaporation, and were heated by means of electron beams that were generated through heating of tungsten filament cathodes. Two independent power supplies were employed to heat the tungsten filaments. The substrates were placed normal to the evaporation sources at a distance of about 40 cm from the source targets. The chamber was evacuated to a base pressure of about 1.33×10^{-5} Pa to 1.33×10^{-4} Pa and an accelerating voltage of about 4 kV was used during evaporation.

During deposition, the film thickness was monitored using two independent quartz crystal thickness monitors for WO_3 and Fe. The metal oxide layer was grown at an average evaporation rate of 1.0 A/s (6 nm/min). The evaporation rate of Fe during co-evaporation with tungsten oxide was about 0.1 A/s (0.6 nm/min). Films about 200 nm thick were deposited at room temperature. Annealing of the WO_3 and

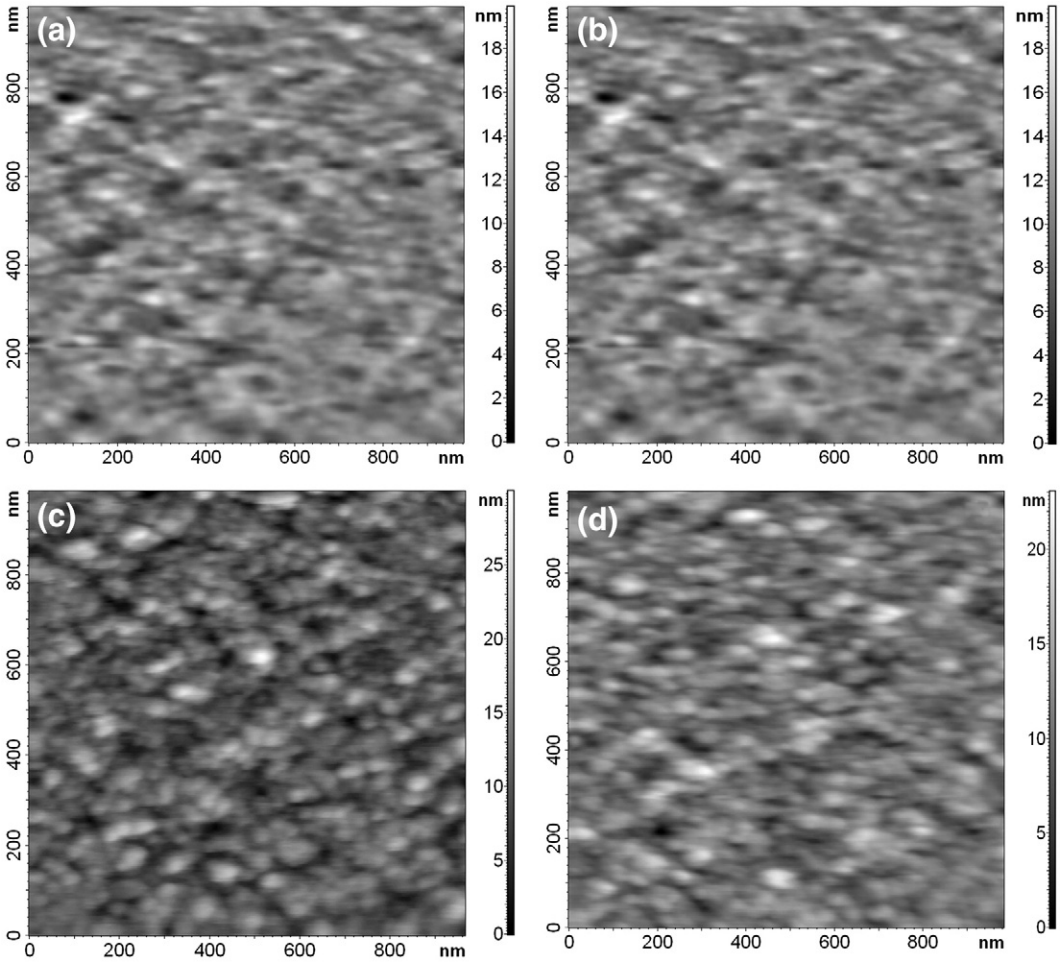

Fig. 1. AFM contact mode images of the surfaces of WO_3 and WO_3:Fe films before (a, c) and after (b, d) heat treatment of the samples in air at 300 °C for 1 h, respectively.