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Gas sensing characteristics of Fe-doped tungsten oxide thin films

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ABSTRACT

This study reports on the gas sensing characteristics of Fe-doped (10 at.%) tungsten oxide thin films of various thicknesses (100–500 nm) prepared by electron beam evaporation. The performance of these films in sensing four gases (H_2, NH_3, NO_2 and N_2O) in the concentration range 2–10,000 ppm at operating temperatures of 150–280 °C has been investigated. The results are compared with the sensing performance of a pure WO_3 film of thickness 300 nm produced by the same method. Doping of the tungsten oxide film with 10 at.% Fe significantly increases the base conductance of the pure film but decreases the gas sensing response. The maximum response measured in this experiment, represented by the relative change in resistance when exposed to a gas, was $\Delta R/R = 375$. This was the response amplitude measured in the presence of 5 ppm NO_2 at an operating temperature of 250 °C using a 400 nm thick WO_3:Fe film. This value is slightly lower than the corresponding result obtained using the pure WO_3 film ($\Delta R/R = 450$). However it was noted that the WO_3:Fe sensor is highly selective to NO_2, exhibiting a much higher response to NO_2 compared to the other gases. The high performance of the sensors to NO_2 was attributed to the small grain size and high porosity of the films, which was obtained through e-beam evaporation and post-deposition heat treatment of the films at 300 °C for 1 h in air.

1. Introduction

Thin film nanostructured metal oxide sensors hold enormous promise to enable a new generation of gas sensing applications due to their ability to near-continuously monitor gases at a large number of locations without the need for additional infrastructure such as power supplies. The gas sensing performance of metal oxide films depends on the reactivity of the film surface, as the mechanism by which gases are detected is based on their oxidizing (e.g. NO_2, N_2O) or reducing (e.g. H_2, NH_3) effect on the surface of the film. The sensing behavior of the metal oxide sensors involves changes in their electrical resistance (conductivity) induced by reactions between the target gases and the film surface. The change in resistance is also influenced by charge transport mechanisms within the film, which are dependent on film properties including grain size, film thickness, film porosity, impurities (dopants), cystallinity and film stoichiometry [1,2]. Nanostructured materials have a very large surface-to-volume ratio and therefore offer more opportunity for surface-gas interaction, and hence enhanced sensing properties. From a theoretical study elsewhere, sensor response can be significantly enhanced if the grain size is smaller than 50 nm [3]. A strong sensing response to sub-ppm concentrations of NO_2 by nanostructured WO_3 films deposited using high vacuum thermal evaporation was shown elsewhere [4]. Tungsten oxide thin films obtained by electron beam evaporation and annealed in the temperature range 350–800 °C for 1–3 h also demonstrated a strong sensing response to NO_2 [5,6]. A 2–3 order increase in response was observed for In_2O_3 films when the grain size was decreased from 60–80 nm to 10–50 nm [7]. Sensors made of WO_3 nanotube have also shown an enhanced response to NO_2 due to the large surface area presented by the interior of the nanotube assemblies [8].

The sensing response of thin films can also be enhanced by impurities, defects and active species on the surface of the film. Dopants are important for the formation of oxygen vacancies, and they also modify the electronic structure and band gap energy of metal oxides. It has been shown elsewhere that metal dopants in the oxide matrix of a thin film increased the film's response to specific gases [9–15]. This effect is due to the consumption of oxygen adsorbates on the metal by reaction with a gas, in addition to the consumption on the metal oxide surface, causing enhanced sensor response. High response and selectivity of WO_3 films doped with Pd to hydrogen gas were reported at a working temperature of 200 °C [16]. The response of WO_3 films to H_2S has been improved by doping with Au, while doping of WO_3 films with Ag and Pt resulted in higher responses to NO_2 and NH_3, respectively [17]. Studies have shown that the addition of Cu to WO_3 thin films improved the sensing response when exposed to NO_2 [18] whereas the addition of Fe

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caused an increase in the response to ozone, CO and ethanol [19]. Defects such as oxygen vacancies are inherent in metal oxides and create a space charge layer depleted of electrons as well as negatively charged oxygen ions on the surface of a thin film. As the metal oxides approach stoichiometry, oxygen vacancies are reduced and the conductivity of the oxide becomes extremely low (high resistance). It has been reported elsewhere that doping of TiO_2 with Fe increases the oxidation activity of the oxide and this has been related to a higher density of oxygen vacancies [20].

Film thickness is another parameter that can have a significant effect on sensor selectivity to different gases as well as sensitivity [21]. Thin films are usually compact, and the active layer is limited to the surface. If a controlled film porosity can be achieved using suitable techniques, then the whole film can potentially interact with the gas species as the gas permeates through the film, and the gas sensing properties can be enhanced significantly [17]. From theoretical and experimental studies, the gas sensing properties of tungsten oxide films are strongly dependent on the relationship between film thickness, crystalline size and Debye length of electrons [6].

Proper control of film thickness, grain size, morphology (effective surface or porosity) and film structure (crystallinity, stoichiometry, composition) is important to achieve a desired sensor performance. Various deposition methods such as sol–gel, CVD, PVD and advanced gas deposition have been used to deposit WO_3 thin films, but each technique has been found to have limitations in achieving the desired film properties for gas sensing applications. Although thermal evaporation can produce porous WO_3 films, it is difficult to control the process, and therefore e-beam evaporation is potentially a more suitable technique. Using e-beam evaporation, nanostructured thin films with ultra-small particles and higher porosity can be obtained. Another factor determining the practical utility of a sensor is its sensitivity at different operating temperatures. Most of the nanostructured metal oxide gas sensors that have been investigated to date are not sufficiently sensitive at lower temperatures (<200 °C) to be used in different applications. The sensors must be thermally activated at elevated temperatures (200–500 °C) to operate, but this leads to a long-term material stability problem due to diffusion and sintering effects. The high operating temperatures of the sensors also demand higher power consumption [22], which makes them unsuitable for battery operated sensing that would be advantageous in some in situ applications.

In the present study, the effect of Fe-doping and film thickness (100–500 nm) on the sensing performance with respect to four gases (H_2, NH_3, NO_2, and N_2O) at concentrations ranging between 2 and 10,000 ppm and at working temperatures between 150 and 280 °C have been investigated. The concentrations (2–10,000 ppm) for the four target gases have been selected to be within the threshold limit values acceptable in various applications (e.g. 25 ppm for NH_3 [17]). The lower operating temperatures (<200 °C) have been selected to investigate the possibility of overcoming stability and high power consumption problems that occur in high operating temperature sensors. The Fe-doped tungsten oxide thin films were prepared by electron beam evaporation, and their physical, chemical and gas sensing characteristics were compared with a pure film of thickness 300 nm deposited by the same technique. It is useful to mention that an optimum film thickness of about 200 nm has been reported for SnO_2 thin films used for CO sensing [21] and similar film thicknesses (200 nm) for pure tungsten oxide have been used in [23]. The 300 nm pure tungsten oxide film showed the best response in previous studies and has therefore been selected in the present study as the standard film for comparison. The microstructure, composition, crystallinity and morphology of the films were analyzed using TEM, AFM, Raman and XPS. The effects of these parameters on gas sensing properties were observed. Particularly, the influence of film thickness and Fe-doping on the gas sensing behavior of tungsten oxide thin films was investigated. The gas sensing properties of Fe-doped tungsten oxide thin films prepared by electron beam evaporation are not well documented in the literature and are worth reporting.

2. Experimental

2.1. Film deposition

Pure (WO_3) and Fe-doped (WO_3:Fe, 10 at.%) tungsten oxide films were deposited by the e-beam evaporation technique (home-made e-beam evaporator, Hokkaido University, Japan) in high vacuum (base pressure of 1.33×10^{-5}–0.133×10^{-5} Pa) at room temperature. Glass and polycrystalline alumina substrates were used for characterization and sensing measurements of the films, respectively. The deposition of the films was performed simultaneously on both substrates to achieve similar film properties, although the different substrates may influence film growth differently. The alumina substrate (dimension: 8 mm × 8 mm) had pre-printed gold-electrodes separated by a distance of 0.3 mm and a pre-printed platinum heating element on its back side. A 99.9% purity WO_3 pellet and 99.95% purity Fe were used as source targets for the e-beam evaporation. The WO_3 pellet 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 e-beam evaporator has dual electron-guns, and two independent power supplies controlled the evaporation rate of the two materials independently. An accelerating voltage of 4 kV was used during the evaporation. The tungsten oxide film was grown at an average evaporation rate of 6 nm/min whereas the evaporation rate of Fe during co-evaporation with tungsten oxide was 0.6 nm/min. The film thickness was monitored using two independent quartz crystal thickness monitors for WO_3 and Fe. Pure and Fe-doped films between 100 and 500 nm were produced. In this paper the results for Fe-doped films of 100, 225, 400 and 500 nm thickness along with a 300 nm thick pure film are reported as these had the best sensing properties. Post deposition annealing of all the films at 300 °C for 1 h in air was performed. It has been reported previously that annealing of WO_3 film at temperatures below 300 °C does not change the particle size significantly [24].

2.2. Film characterization

The cross-sectional view of the films was investigated using a Jeol 2010F Transmission Electron Microscope with an EDX system at an accelerating voltage of 200 kV. The main features that were investigated using this technique were the cross-sectional view of the films and the crystalline structure of the films. The morphology and average grain size of the films were obtained using an NT-MDT Solver P47 scanning probe microscope (NT-MDT Co., Moscow, Russia) operated using AFM contact mode with "Golden" Si cantilevers. The AFM scans were performed using a silicon tip with nominal tip radius of curvature of 10 nm. The mean grain size and surface roughness were determined using the Nova NT-MDT Image Analysis Software.

The chemical properties of the films were obtained using X-ray photoelectron spectrometer (XPS). Data were acquired using a Kratos Axis ULTRA XPS incorporating a 165 mm hemispherical electron energy analyser. The incident radiation was monochromatic Al Kα X-rays (1486.6 eV) at 150 W (15 kV, 10 mA) and at 45° to the sample surface. Photoelectron data was collected at a take off angle of theta = 90°. 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 taken at 20 eV and run with 0.05 eV steps and 250 ms dwell time. Base pressure in the