Conductometric Gas Sensors based on Nanostructured WO_3 Thin Films

M. Ahsan, T. Tesfamichael and Prasad KDV Yarlagadda
Science and Engineering Faculty
Queensland University of Technology
Brisbane, Queensland.
y.prasad@ut.edu.au

***Abstract*—Nanostructured WO_3 thin films have been prepared by thermal evaporation to detect hydrogen at low temperatures. The influence of heat treatment on the physical, chemical and electronic properties of these films has been investigated. The films were annealed at 400°C for 2 hours in air. AFM and TEM analysis revealed that the as-deposited WO_3 film is high amorphous and made up of cluster of particles. Annealing at 400°C for 2 hours in air resulted in very fine grain size of the order of 5 nm and porous structure. GIXRD and Raman analysis revealed that annealing improved the crystallinity of WO_3 film. Gas sensors based on annealed WO_3 films have shown a high response towards various concentrations (10-10000 ppm) H_2 at an operating temperature of 150°C. The improved sensing performance at low operating temperature is due to the optimum physical, chemical and electronic properties achieved in the WO_3 film through annealing.**

Keywords-nanostructured; thin films; WO_3; thermal evaporation; annealing.

I. INTRODUCTION

Gas sensors operate on the principle of conversion of gas concentration into a measurable signal. Gas sensor devices that have been developed so far include mass sensitive sensors, optical sensors, electrolytic sensors and solid state sensors [1]. Among the solid-state gas sensors, semiconductor metal oxide gas sensors have received the most attention as they show good potential for continuous monitoring of gases. These sensors offer a wide variety of advantages over the traditional analytical instruments which include lower cost, easier manufacturing, smaller size, short response and faster recovery. Semiconductor metal oxide material such as tungsten oxide (WO_3) has shown great potential for gas sensing due to its inherent electrical conductivity and excellent sensitivity towards various gases. Low fabrication costs combined with low power consumption and a promise of high gas sensitivity towards specific gases are the driving force behind research on WO_3 for improved gas sensing properties. However, as for any other metal oxide based gas sensor, WO_3 based gas sensors operate efficiently only in the temperature range 200°C-500°C [2].

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 [3] and type of metal oxide (n-type or p-type). For n-type sensor material like WO_3 and a reducing gas, 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. 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 towards sub-ppm concentrations of NO_2 [4]. Mesoporous nanostructured WO_3 films have shown a high sensitivity to NO_2 even at low concentrations [5]. WO_3 thin films with smaller grain size obtained by rf sputtering have shown enhanced sensitivity to oxidizing gases [6]. Annealing of WO_3 films after deposition has been reported to improve crystallinity and defined grain boundaries in the film [7-9].

The aim of this paper is to investigate the gas sensing performance of thermally evaporated WO_3 films at low operating temperatures by optimizing the physical, chemical and electronic properties of these films.

II. EXPERIMENTAL METHODS

WO_3 thin films were deposited on silicon substrate (8 mm x 8 mm x 0.5 mm) with interditigated Pt electrodes using thermal evaporation technique. Tungsten oxide (99.9% purity, 20 μm) was used as evaporation source. Before the deposition, the powder was placed in dessicator to avoid any moisture and decontamination. 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 per second. A quartz crystal film thickness monitor was used to control the thickness of films which was restricted to 300 nm.

After the deposition, the films were annealed at 400°C for 2 hours in air to improve the microstructural properties and relieve any thermal stresses in the films.

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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 500 nm^2 to 2000 nm^2. The mean grain size and grain distribution and surface roughness were determined by using the Nova NT-MDT Image Analysis Software. A Jeol 1200 TEM was used at an accelerating voltage of 120kV to investigate the shape and size of WO_3 nanoparticles. Samples were investigated by scratching the film and placing it on TEM grid. 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^o and the 2θ range was kept between 10^o to 85^o with a step size of 0.05^o. The WO_3 sensor responses to various concentrations (10-1000 ppm) of hydrogen at various operating temperatures (100^oC to 300^oC) were measured. Hydrogen was diluted in synthetic air to achieve the desired concentrations. For all the experiments, the total flow was adjusted to 200 sccm. The gas sensing performance of the films to reducing gases such as H_2 denoted as $S_{reducing}$ is defined as the ratio:

$$S_{reducing} = \frac{R_{air} - R_{gas}}{R_{gas}} X\,100 \qquad (1)$$

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. Equation 1 can be applied for n-type material such as WO_3 and reducing gas such as H_2.

The response curve was recorded under a continuous flow of known amount of H_2. A sequence control computer was utilized to computerize the pulse sequence of the H_2 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 minutes 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^oC to 300^oC at intervals of 50^oC under various concentrations of H_2, and optimum operating temperature was determined. This was followed by two full range tests for each sensor and H_2 at the optimum operating temperature.

III. Results And Discussions

The surface topography of as-deposited WO_3 film is shown in Figure 1. The mean particle size and roughness were found to be 13 nm and 0.5 nm respectively, as determined from Nova NT-MDT Image Analysis Software. Upon annealing at 400^oC for 2 hours in air, a very grain size (5 nm) and porous structure are observed (Figure 2). It appears that the as-deposited WO_3 film is made up of cluster of small particles. The nucleation and successive grain growth as a result of annealing at 400^oC for 2 hours in air transformed these particles into very fine grains and well defined grain boundaries.

Figure 3 shows the GIXRD patterns of as-deposited and annealed WO_3 films. The as-deposited film did not show any diffraction pattern, which indicates that as-deposited film is highly amorphous. However, after annealing at 400^oC, significant crystallinity is observed in the films, indicated by appearance of diffraction peaks in GIXRD pattern. The peaks obtained at $2\theta = 24.112^o$, 28.538^o, 34.361^o, 41.615^o, 49.843^o, 55.684^o, 61.941^o are closely related to monoclinic WO_3 phase [10]. It should be noted that the lattice parameters of orthorhombic WO_3 phase are very similar to monoclinic phase,

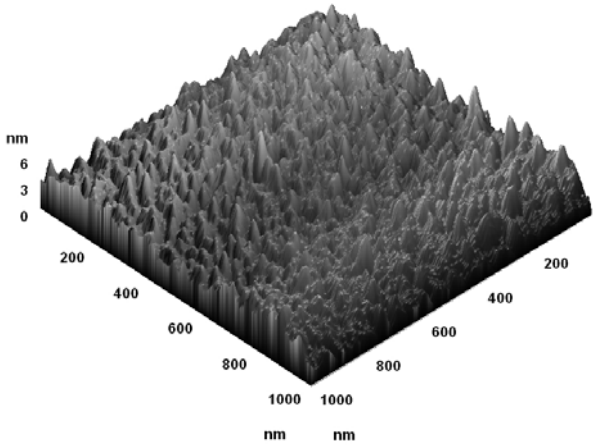

Figure 1. AFM topography image of as-deposited nanostructured WO_3 thin film.

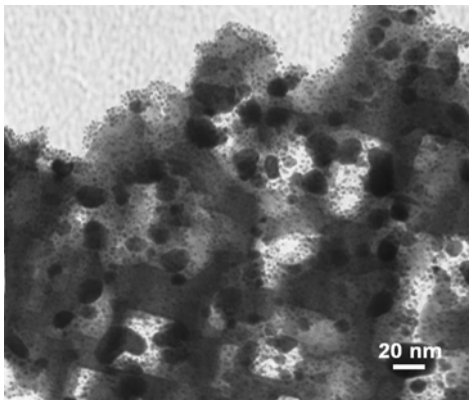

Figure 2. TEM image of nanostructured WO_3 thin film annealed at 400^oC for 2 hours in air.

and thus, these two phases cannot be distinguished within the accuracy of GIXRD data. It has been reported that the two intense peaks observed at $2\theta=24.278^o$ and 34.117^o are associated to (2 0 0) and (2 2 0) monoclinic planes of WO_3 corresponding to $d=3.663^o$ and 2.626 Å, respectively [11]. The lattice parameters were found to be a = 7.375 Å, b = 7.375 Å and c = 3.903 Å and its unit cell volume is about 212.38 $Å^3$.

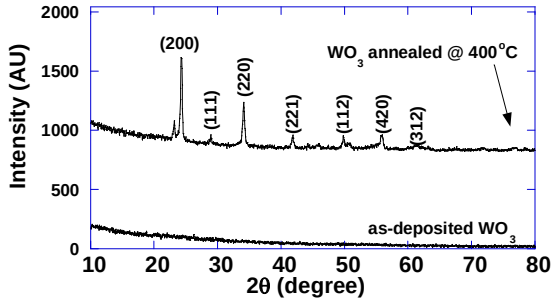

Figure 3. GIXRD spectra of as-deposited and annealed WO_3 thin films.

The Raman spectra of as-deposited and 400°C annealed films are shown in Figure 4. Two characteristic Raman bands are associated with WO_3. The first band lies between 200-500 cm^{-1} and is associated with O-W-O bending vibration modes. The second band lies in the range 600-1000 cm^{-1} and is associated with W-O stretching vibration modes. The as-deposited WO_3 film exhibited weak and broad Raman bands centred at 315 cm^{-1} and 799 cm^{-1}. These features are characteristic of amorphous materials and are usually assigned to O-W-O deformation modes and O-W-O stretching vibration modes of monoclinic WO_3 phase, respectively [12]. This is in accordance with the GIXRD observations. However, crystallinity of the WO_3 increased after annealing at 400°C, as shown by sharp peaks at 707 cm^{-1} and 799 cm^{-1} which are characteristic of O-W-O stretching vibration modes [13]. Raman results indicate that the annealed films are highly crystalline, which is also supported by GIXRD observations.

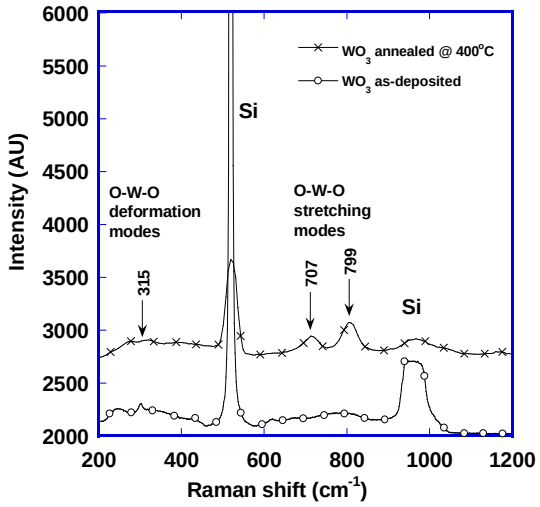

Figure 4. Raman spectra of as-deposited and annealed WO_3 thin films.

The as-deposited films did not show any response towards H_2 in the selected temperature range. It has been shown experimentally that amorphous films have poor sensor response characteristics [14]. The amorphous nature of the as-deposited films seems to lead these films being not suitable for gas sensing. When the film is annealed at 400ºC, an optimum response is obtained at an operating temperature of 150ºC (Fig. 5). A high sensitivity S=10 to 10,000 ppm H_2 is observed. The response and recovery time to 10000 ppm H_2 are 140 s and 80 s at 150ºC.

WO_3 is an n-type semiconductor material and commonly operates as a gas sensor in the temperature between 200°C - 500°C [15]. When it is exposed to a reducing gas such as H_2, the oxygen adsorbates on the film surface interact with the gas and release electrons back to the film, causing a drop in film resistance. However, the opposite behaviour (i.e. an increase in resistance) is observed for the 400ºC annealed WO_3 film upon exposure to H_2 at 150ºC. Such behaviour cannot be explained by merely considering the microstructural properties such as grain size and porosity of the film.

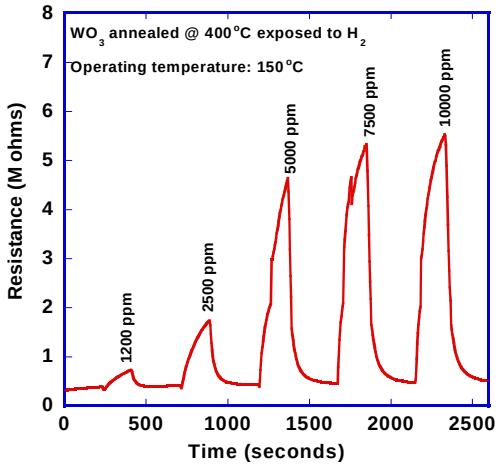

Figure 5. Dynamic response of 400°C annealed WO_3 thin film upon exposure to H_2 at 150°C.

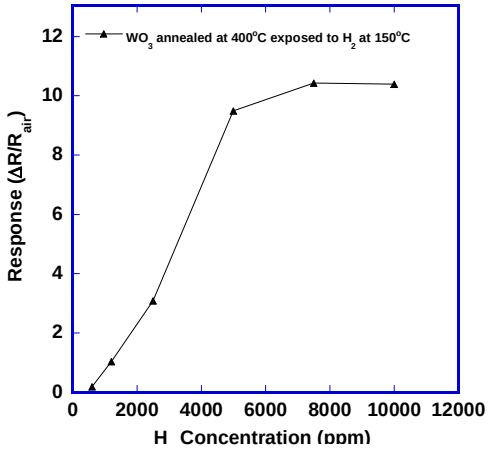

Figure 6. Response amplitude of 400°C annealed WO_3 film upon exposure to H_2 at 150°C.

In polycrystalline materials, surface barriers which electrons have to overcome for taking part in the conduction are formed at the intergranular surfaces. The height of surface barrier depends on the concentration of charge carriers (oxygen adsorbates) at the surface, and, therefore, overall resistance changes can be correlated with changes in surface band bending. The overall resistance, and, hence, surface band bending increased exponentially when the polycrystalline WO_3 surface was exposed to increasing concentrations of oxygen [16]. The increase in resistance observed for the 400ºC annealed WO_3 film exposed to H_2 at an operating temperature of 150ºC might arise from various forms of oxygen adsorbates (O^-, O^{2-} and O_2^-) on WO_3 surface, which depend on temperature. At 150ºC, the most dominant form of adsorbed oxygen is O_2^- [17]. Upon exposure to H_2, the O_2^- species dissociates into O^- with the formation of water, as per the following equation.

$$H_2 + O_2^- \rightarrow H_2O + O^- \qquad (2)$$

Insitu Raman analysis of WO_3 films annealed at 300ºC and 400ºC has shown that the rate of water desorption above 100ºC is much faster than the rate of water formation on the film surface when WO_3 film is exposed to H_2 [18]. At 150ºC, the high concentration range of H_2 (600 ppm – 10000 ppm) produces more O^- species on the surface, leading to increase in surface barrier height, consequently increasing the resistance. Hence, this can be a reason why an increase in resistance was observed at lower operating temperature. The high sensitivity to H_2 at 150ºC observed for the 400ºC annealed WO_3 film is attributed to its very small grain size (5 nm), porous structure and high crystallinity.

IV. Conclusions

Nanostructured WO_3 thin films have been deposited using thermal evaporation technique. The as-deposited films are highly amorphous and made up of cluster of particles. Annealing these films at 400ºC for 2 hours in air improved the crystalline and transformed these clusters into very small grains of 5 nm size and a porous structure. The GIXRD and Raman analysis show that annealing improves the crystallinity of these films. The annealed WO_3 film shows a high response to various concentrations of H_2 at a relatively low temperature of 150ºC. The response to hydrogen is mainly attributed to the very small grain size, porous structure and high crystallinity achieved by heat treatment.

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Professor Prasad Yarlagadda has worked in industry and universities for over 27 years in India, Hong Kong, Singapore, Papua New Guinea, and Australia. He was Founding Director of Smart Systems Research theme (2005-2009) in QUT. At Present he is Project Director, Airport of the Future project which is multi-disciplinary research project in the field of airport security, facilitation, risk and continuity planning. Prof. Yarlagadda has published more than 325 quality papers in high quality international Journals and conference proceedings. At present he is Editor-in-Chiefm GSTF Journal of Engineering Technology, s Deputy Editor-In Chief of International Journal of Advances in Manufacturing and Materials Engineering and was also guest editor to number of international journals. He received significant amount of research funding from various government and industrial organizations. Prof. Yarlagadda received number of awards from various national and international agencies for his outstanding contribution to engineering field in particular to discipline of manufacturing. He recently received Fryderyk Staub Golden Owl Award from World Academy of Manufacturing and Materials, Poland, for his outstanding contribution to the discipline of materials and manufacturing engineering in the international arena. He is a fellow of professional organizations such as Institution of Engineers, Australia, World Academy of Manufacturing and Materials Engineering (Poland), Institution of Engineers, India, Society of Manufacturing Engineers, USA, American Society of Mechanical Engineers, USA, Institution of Mechanical Engineers, UK and Society of Professional Engineers, PNG. Currently Prof. Yarlagadda is leading a team of researchers in both Aviation security and also Manufacturing applications for Biomedical Engineering and other related applications. More recently in 2012 Prof. Yarlagadda received a Prestagious Great Honour Award for his outstanding and life time contribution to the discipline of manufcturing and materials engineering in world Areana from World Academy of Manfuacturing and Materials and Materials Division of Polish Academy of Sciences. In 2013, he also got appointed as Deputy Chair Person, Science and Technology Committee on GOPIO International.