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Gas sensing of ruthenium implanted tungsten oxide thin films

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ABSTRACT

Different amounts of Ru were implanted into thermally evaporated WO_3 thin films by ion implantation. The films were subsequently annealed at 600 °C for 2 h in air to remove defects generated during the ion implantation. The Ru concentrations of four samples have been quantified by Rutherford Backscattering Spectrometry as 0.8, 5.5, 9 and 11.5 at.%. The un-implanted WO_3 films were highly porous but the porosity decreased significantly after ion implantation as observed by Transmission Electron Microscopy and Scanning Electron Microscopy. The thickness of the films also decreased with increasing Ru-ion dose, which is mainly due to densification of the porous films during ion implantation. From Raman Spectroscopy two peaks at 408 and 451 cm^{-1} (in addition to the typical vibrational peaks of the monoclinic WO_3 phase) associated with Ru were observed. Their intensity increased with increasing Ru concentration. X-ray Photoelectron Spectroscopy showed a metallic state of Ru with binding energy of Ru $3d_{5/2}$ at 280.1 eV. This peak position remained almost unchanged with increasing Ru concentration. The resistances of the Ru-implanted films were found to increase in the presence of NO_2 and NO with higher sensor response to NO_2. The effect of Ru concentration on the sensing performance of the films was not explicitly observed due to reduced film thickness and porosity with increasing Ru concentration. However, the results indicate that the implantation of Ru into WO_3 films with sufficient film porosity and film thickness can be beneficial for NO_2 sensing at temperatures in the range of 250 °C to 350 °C.

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1. Introduction

Transition semiconducting metal oxides such as SnO_2, ZnO, TiO_2, In_2O_3, Fe_2O_3, WO_3 and MoO_3 have been widely investigated for gas sensing devices because of their simplicity and low cost [1–12]. The most common sensing mechanism of the metal oxide sensors involves the changes in the electrical resistance induced by reactions between the target gas and the film surface [13]. These reactions cause injection or extraction of electrons from the metal oxide, changing the resistance of the material. The semiconducting oxides show good chemo-sensitivity towards oxidizing and reducing gases and have been widely used for sensing various gases and vapors. Key sensor response parameters, characterizing the sensing behavior of the metal oxide sensors, are the sensor response (sometimes denoted as sensitivity), the response and recovery times and the selectivity. The sensor response of n-type semiconducting metal oxides (e.g. WO_3) in oxidizing gases such as NO and NO_2 [12] can be defined as R/R_0; where R_0 and R are the steady state resistance values achieved within reasonable time during the exposure of the sample to the reference gas (synthetic air) and the target gas, respectively. The response (τ_{RESP}) and recovery (τ_{REC}) times are important sensor characteristics. τ_{RESP} here is defined as the time the sensor resistance takes to reach the 90% of its final value, and τ_{REC} as the time the sensor response takes to recover the 90% of its baseline value. The sensor performance (i.e. sensor response, response time and recovery time) is highly dependent on the film characteristics (electronic properties, crystallinity, grain size, defect structure, vacancies, porosity, film thickness, film stoichiometry, and surface morphology). These factors can be controlled by changing the deposition conditions, the post-deposition annealing, and doping [3,12,14,15].

Thin films of tungsten oxide (WO_3) deposited by Physical Vapor Deposition techniques are very promising for gas sensing due to the intrinsic electronic properties of the material. In fact, tungsten oxide has a good response towards various gases at lower operating temperatures because of a slight substoichiometry [16–19]. The material behaves like an n-type semiconductor because of its non-stoichiometry, predominantly due to defects in oxygen vacancies. As the metal oxide approaches stoichiometry, the conductivity change of the material due to target gas can be very low and hence a reduction of the sensor response is obtained. Sensor response can be enhanced through tailoring and optimizing nanostructural parameters such as particle size, surface morphology, film thickness and porosity. Porous nanostructured materials have a very large surface-to-volume ratio

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offering more surface/gas interaction and thereby enhance both sensor response and response time significantly [20]. Several theoretical studies [21,22] have shown that the sensor response can be significantly enhanced if the grain size is smaller than 50 nm as confirmed by previous work [17,19]. Sensors made of WO_3 nanotubes have also shown enhanced gas response due to the large surface area presented by the interior of the nanotube assemblies [23]. Metal inclusions are important for the formation of oxygen vacancies, modification of the electronic structure, and band gap energy of metal oxides in order to enhance response to target gases [24–26]. In most of the literature, doping concentration has been limited to about 5 wt.% [27], but higher values (up to 25 wt.%) have been shown to improve the sensing performance [28]. Metal doping can also change the response to specific gases by increasing the sensor response to specific gases (i.e. selectivity) [29]. High response and selectivity of Pd-doped WO_3 films to H_2 gas have been reported at a working temperature of 200 °C [30]. The response of WO_3 film to NO_2 and NH_3 has been improved when doped with Ag and Pt, respectively [31]. Studies have shown that the addition of Cu to WO_3 thin film improved the sensor response when exposed to NO_2 [32], whereas the addition of Fe increased the response to ozone, CO and ethanol [33]. It has been reported that doping of TiO_2 film with Fe increased the oxidation activity of the oxide and this has been related to a higher density of oxygen vacancies [28]. Film thickness is another parameter that can have significant effect in optimizing sensor selectivity and response [34,35]. 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 [12]. Tungsten oxide thin films obtained by electron beam evaporation and annealed in the temperature range of 350–800 °C for 1–3 h also indicated highly effective gas sensing properties to NO_2 [11].

The gas sensing properties of Ru implantation WO_3 thin films are not documented in the literature. Ruthenium does not oxidize easily and its oxides have different properties: conducting oxide (RuO_2) and oxidizing agents in organic compounds (RuO_4) [36]. It has been reported that doping of nanostructured thin SnO_2 films with Ru strongly enhanced the response towards gaseous NO_2 [37]. In this paper, the chemical and physical properties of various Ru-implanted tungsten oxide thin films have been characterized in order to understand the interaction between the Ru and the WO_3 on the nanoscale. Different techniques including Rutherford Backscattering Spectrometry (RBS), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy have been used. In addition, we report the gas sensing characteristics of the films to NO and NO_2 by measuring the resistance change of the films during repeated exposure to the target gases.

2. Experimental

2.1. Sample preparation

Thin films of tungsten oxide were deposited on Si-substrate using thermal evaporation. Commercial powder of tungsten oxide (99.9% purity, average powder size 20 μm) was used for the evaporation. Single crystalline Si with about 300 nm SiO_2 top layer and interdigitated Pt electrodes printed on this layer (purchased form Electronics Design Center, Case Western Reserve University, Cleveland, USA) has been used as a substrate. The effective area of the interdigitated electrodes was 8 mm × 8 mm. The electrode fingers had a line width and height of 100 μm and 300 nm, respectively. A bell jar type thermal evaporator unit (Varian Coater with Control System designed by AVT Pty Ltd, Australia) was used to deposit the WO_3 thin films. The substrate was placed at a distance of 38 cm in line of sight from the evaporation source. Deposition was carried out in high vacuum at 4×10^{-3} Pa with an evaporation rate of 35 nm/s. A quartz crystal film thickness monitor was used to achieve the desired thickness of the films. The WO_3 film sample preparation using thermal evaporation used in this experiment has been described in previous work [17].

These films were implanted with Ru using a direct extraction metal ion source, in a vacuum chamber, which was evacuated to a base pressure of about 3×10^{-4} Pa. After achieving the required vacuum, a high current was applied to the Ru cathode to generate a Ru ion beam that was accelerated at a voltage of 20 kV. The charge state distributions of Ru in the ions were: $Ru^{+1} = 0.4\%$; $Ru^{+2} = 17\%$; $Ru^{+3} = 75\%$; $Ru^{+4} = 7\%$; $Ru^{+5} = 0.6\%$ with an average energy of about 60 keV and an average range of about 25 nm. Different Ru ion doses (10^{15}–5×10^{17} cm^{-2}) were obtained by varying the implantation time. Uniformity of the implantation was assured by sweeping the sample across the ion beam. After ion implantation, the films were annealed at 600 °C for 2 h in air to relieve the stress generated by ion implantation and improve the crystallinity of the films.

2.2. Sample characterization

RBS measurements were carried out to determine the concentration profile of Ru in the WO_3 films. A 1.8 MeV He^+ beam under a vacuum of 7×10^{-4} Pa was applied to the samples. The experimental data were fitted using SIMNRA software. The software is based on Microsoft Windows program and commonly applied for the simulation of backscattering spectra for ion beam analysis with MeV ions. A JEOL 1200 TEM was used at an accelerating voltage of 120 kV to investigate the cross-sectional area of the films in order to determine porosity, film thickness, and crystalline structure. During the TEM analysis, X-ray mapping has been applied to observe the distribution of the implanted Ru across the WO_3 film. The surface morphology and grain distribution of the films were obtained using a ZEISS SIGMA FE-SEM.

XPS analysis of the films were 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, incident at 45° to the sample surface. Photoelectron data were collected at a take-off angle of 90°. Survey scans were taken at analyzer pass energy of 160 eV and multiplex-high resolution scans at 20 eV. The survey scans were carried out over 1200 to 0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms, whereas narrow high-resolution scans were run with 0.05 eV steps and a 250 ms dwell time. Base pressure in the analysis chamber was kept at 1.0×10^{-7} Pa and during sample analysis at 1.0×10^{-6} Pa. The bonding and crystal structure of the Ru-implanted WO_3 films were analyzed using a Renishaw System-1000 Raman Spectroscopy. A HeNe laser excitation source of wavelength 633 nm with a 5 mW power at the sample was used. A Raman shift between the wavenumbers of 200 and 1200 cm^{-1} has been measured. A single crystal silicon wafer was used as a reference.

To monitor the gas-dependent resistances, the deposited Ru implanted WO_3 thin films were installed in a quartz-tube furnace with an inner diameter of 22 mm and 250 °C and 350 °C were selected as operating temperatures. The sensing properties of Ru implanted WO_3 were investigated in the presence of low concentration of NO and NO_2 target gases (0.25–2 ppm) in a 2 l/min gas flow of 20% O_2 balanced with N_2. The gas exchange time of the system is in the range of 7 s and the NO and NO_2 concentrations were validated by a Chemiluminescence Detector (700 EL ht, Ecophysics, resolution 0.1 ppm). NO and NO_2 were applied alternately. A 2 ppm NO was added to the gas stream for 30 min followed by 30 min without NO, while periods with up to 2 ppm NO_2 lasted for 45 min followed by 75 min without NO_2.

During exposure to NO and NO_2, the electrical impedance of the films was recorded time-continuously at a frequency of 10 Hz and an applied voltage (rms) of 0.1 V by an impedance analyzer (Alpha High Performance Frequency Analyzer, Novocontrol). The resistance *R* was

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