Electronic Transport Mechanisms in WO_3-Based Ultra-Thin Film Chemiresistive Sensors

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SUMMARY

A variety of WO_3 thin film structures were produced on sapphire substrates under controlled physical vapor deposition. Direct correlations were found between deposition parameters, microstructure, and electrical response both in vacuum and in the presence of test gases. Carrier concentration data indicate that WO_3 becomes substoichiometric in vacuum and electronic transport is dominated by oxygen vacancy states, while in atmospheric air and/or oxidizing gases, the vacancy concentration becomes smaller and other defect states become important. Hall mobility data reveal that charge scattering mechanisms (hopping vs. impurity vs. phonon) depend on the crystallographic phase and microstructure of the WO_3 film.

Keywords: Tungsten Oxide, Chemiresistive Sensor, Electronic Transport

INTRODUCTION

Chemiresistive gas sensors based upon semiconducting metal oxide (SMO) films containing catalytic particles are generally sensitive and selective to a wide variety of target gases. However, important characteristics necessary for reliable commercial applications including reproducibility, baseline stability, rapid response time, and interferent rejection need to be improved. Each of these characteristics is strongly dependent on the specific film microstructure, charge transport within the film, and oxide surface chemistry.

Highly porous SMO thick films are typically used in commercially available chemiresistive sensors, but these thick film sensors exhibit limitations in terms of long term stability and drift in baseline conductivity. Our work has emphasized ultra-thin tungsten oxide films produced under controlled conditions [1,2] in order to obtain well-defined microstructures that potentially can yield stable highly selective and sensitive microsensors.

Tungsten oxide crystallizes in a distorted rhenium oxide cubic structure. The distortion is temperature dependent and leads to several closely related WO_3 structures (e.g. monoclinic, tetragonal, orthorhombic) which result from slight rotations of $<WO_6>$ octahedral units with respect to each other [3]. Stoichiometric WO_3 readily loses oxygen to form a WO_{3-x} lattice via the formation of vacancy and crystallographic shear plane defects [4]. It is this nonstoichiometry that gives rise to the chemiresistive gas sensing mechanism: physisorption or chemisorption reactions on the WO_3 surface create and/or annihilate oxygen vacancies or interstitial cations within the oxide film changing its conductivity.

In this work, we have synthesized ultra-thin WO_3 films (<300 nm thickness) containing a variety of well-defined microstructures on atomically smooth r-cut sapphire substrates using molecular beam epitaxy (mbe) techniques, and have characterized them *in situ* using a newly constructed ultra-high vacuum (UHV) based Hall effect apparatus (Figure 1) [5].

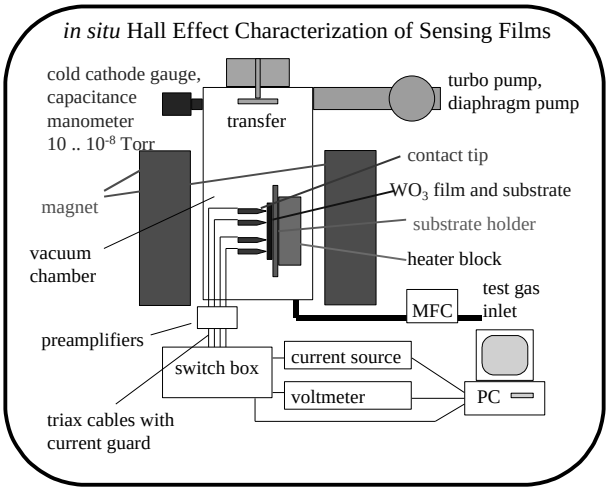

Fig. 1: *Schematic of Hall effect testing system that allows in situ electrical characterization immediately after film deposition in UHV and in controlled gases up to atmospheric pressure.*

EXPERIMENTAL

The WO_3 films were grown using both RF magnetron sputtering and electron cyclotron resonance (ECR) oxygen plasma-assisted evaporation on r-cut sapphire wafers with *in situ* RHEED monitoring of film structure. Deposition parameters that were found to strongly influence film characteristics (i.e. phase, microstructure, stoichiometry) include deposition temperature, deposition rate, and plasma gas composition [1,2]. Post-deposition annealing treatments either in UHV or controlled atmospheres also yielded unique film microstructures. Films were transferred in UHV directly after growth into the Hall effect chamber for subsequent gas / thermal processing and electronic characterization.

FILM MICROSTRUCTURE

In this work, we concentrated on films that consisted of either the monoclinic or tetragonal phase of WO_3. The as-deposited films were synthesized to be stoichiometric within the detectability limit of X-ray photoelectron spectroscopy (XPS). Reduced oxide stoichiometries were obtained through careful post-deposition thermal treatments in UHV or in well-defined partial pressures of O_2 or laboratory grade dry air.

Figure 2 shows x-ray diffraction (XRD) data illustrating crystallographic texture that can be produced for monoclinic phase WO_3, ranging from epitaxial to highly oriented to random polycrystalline. XRD pole figures (not shown) have been used to quantify the degree of crystallographic texture.

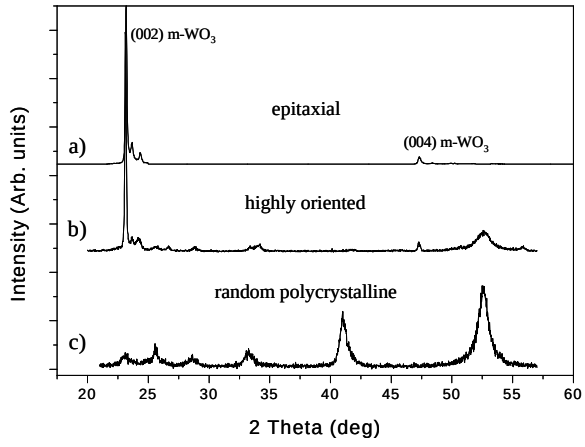

Fig. 2: *X-ray diffraction spectra showing three different film microstructures that can be produced for monoclinic phase WO_3 films.*

RHEED analysis during film growth indicated that highly epitaxial films can be grown on r-cut sapphire substrates for deposition rates between 1 to 6 nm/min. The tetragonal WO_3 phase formed at 450°C growth temperature, whereas at 600°C the monoclinic WO_3 phase was produced as shown in Figure 3. Due to a slight mismatch with the r-cut sapphire lattice, the epitaxial films contained 'granular' microstructure under imaging by scanning tunneling microscopy (STM). However, each grain had essentially the same orientation as determined from RHEED and XRD pole figure analysis, in contrast to random polycrystalline films formed by deposition < 200°C followed by annealing in the 450 – 600 °C range. Since the lattice parameters for the monoclinic phase are nearly equal [3] three possible {200}-like orientations (Figure 3b) are distinguishible by XRD.

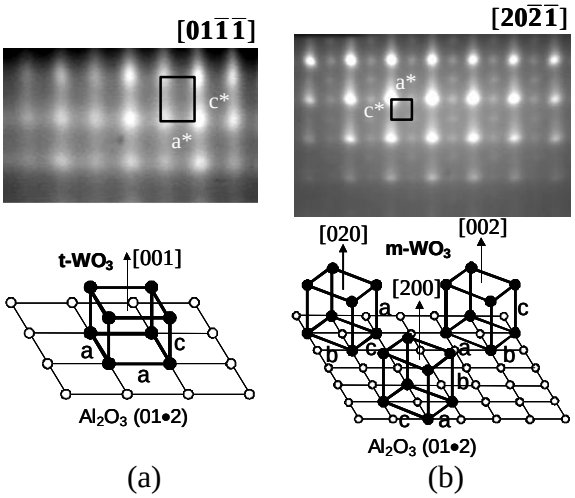

Fig. 3: *RHEED transmission diffraction patterns and corresponding epitaxy models from (a) tetragonal phase WO_3 grown at 450°C and (b) monoclinic phase WO_3 grown at 600°C .*

ELECTRONIC TRANSPORT

Using spring-loaded probe contacts in the Hall effect apparatus using Van der Pauw geometry, carrier concentration and Hall mobility were measured as a function of temperature over the range 25 – 400 °C. Figure 4 shows this temperature dependence for epitaxial monoclinic WO_3, epitaxial tetragonal, and polycrystalline monoclinic WO_3, all annealed for 5 hrs at 400 °C and measured in a UHV environment. The carrier concentration is nearly linear and reversible for each of the films types when plotted on a *log n* vs. *1/T* plot; the activation energies were measured to be ~ 0.15

eV suggesting that conductivity is dominated by a vacancy-induced state within the band gap of the reduced WO_{3-x} films.

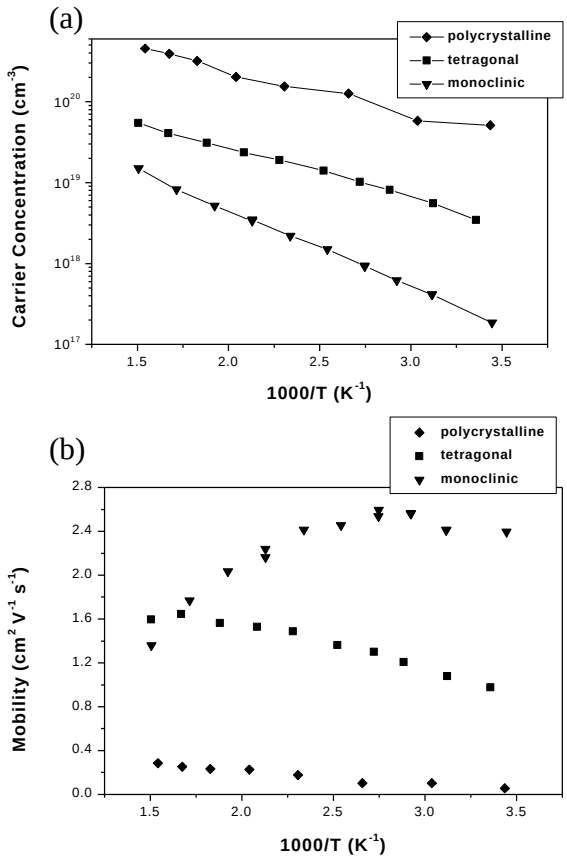

Fig. 4*: (a) Apparent carrier concentration and (b) Hall mobility measured as a function of inverse temperature for WO_3 films annealed and measured in UHV. All measured Hall coefficients were negative in sign indicating electrons as majority carriers.*

We have measured variations in the Hall mobility as a function of phase and crystallographic texture, and each of the values is very small (<3 $cm^2V^{-1}s^{-1}$). The mobility of the monoclinic phase decreases with increasing temperature consistent with a phonon scattering mechanism. This behavior is similar to data reported for a slightly reduced WO_{3-x} single crystal [6]. However, the tetragonal phase mobility increases with temperature suggestive of a hopping conduction mechanism [7]. This hopping behavior may be derived from the increased number of grain boundaries and smaller grain size as observed by STM and XRD, or from the different crystal structure itself. The very small mobility of the polycrystalline monoclinic phase and its increase with temperature is consistent with a microstructure containing a high density of grain boundaries and crystallographic defects.

The same electronic transport measurements were carried out in laboratory-grade 100% dry air at atmospheric pressure. After annealing the films for 5 hours at 400 ^oC, the films were too resistive to get good signal to noise levels for Hall measurements. Therefore, only Van der Pauw conductivity results were acquired (Figure 5). The monoclinic phase shows two linear regimes for the temperature activated conductivity, ~0.37 eV at low temperature and ~0.14 eV above 215^oC. The similarity in slope with the vacuum measurements imply that vacancy-induced charge carriers become dominant at higher temperature. However, the vacancy concentration is low enough such that vacancy states are masked by other defects contributing to the carrier concentratrion at lower temperature.

Compared to the monoclinic phase, the conductivity of the tetragonal phase and the random polycrystalline monoclinic structure is at least an order of magnitude smaller. The turn over in slope at high temperature for the tetragonal film may be indicative of microstructural changes upon heating; this has not yet been verified.

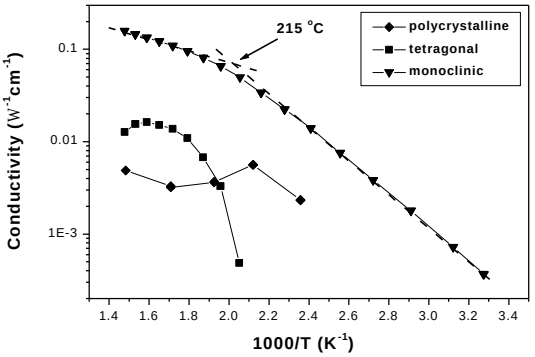

Fig. 5: *Van der Pauw conductivity measured as a function of inverse temperature for WO_3 films annealed and measured in dry air.*

Figure 6 shows the responses of the tetragonal and monoclinic WO_3 phases to an initial dose of 200 parts-per-million H_2S gas in dry air carrier gas at 250^oC. The lower baseline conductivity of the tetragonal phase yields a much larger sensor response upon H_2S exposure. However, the slower response of the tetragonal phase correlates with lower measured Hall mobilities compared to the monoclinic phase. Similar correlations of response time to film microstructure have been observed with exposure to H_2O, O_2, and methanol

gases. Preliminary Hall effect measurements on WO_3 films containing CuO, SnO_2, and TiO_2 catalyst additives being carried out in our lab suggest that charge transport dynamics can differ significantly in these systems.

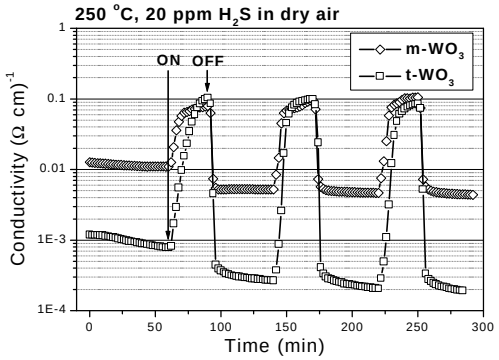

Fig. 6: *Film responses to 20ppm H_2S target gas for epitaxial monoclinic and tetragonal WO_3 phases.*

ACKNOWLEDGMENTS

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