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Synthesis and structural characterization of tungsten trioxide nanoplatelet-containing thin films prepared by Aqueous Chemical Growth☆

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ABSTRACT

We report the synthesis of WO_3 thin films predominantly made up of nanoplatelets, on transparent plain glass microscope slides, by the low-temperature, soft chemistry method of Aqueous Chemical Growth (ACG). During the heterogeneous growth, by ACG, of WO_3 thin films onto these plain glass substrates, nanoplatelet and nanorod-like structures of WO_3 were also precipitated out of the Peroxotungstic acid precursor solutions and collected as slurries which were annealed at 500 °C to give ultra-fine powders of WO_3. Scanning Electron Microscopy of the thin films and powders showed that nanoplatelets formed had thicknesses generally less than 300 nm and lengths and diameters in the 1–2 μm range. The thin films formed were less than 5 μm thick. Transmission Electron Microscopy (TEM) on one of the thin films confirmed the formation of nanoplatelets as well as nanorod-like structures, while High Resolution TEM alongside X-ray Diffraction and Raman spectroscopy suggested that the WO_3 thin film grown on a plain glass microscope slide was monoclinic in crystal structure. While Energy Dispersive X-ray Spectroscopy, Fourier Transform-Infrared Spectroscopy, and Attenuated Total Reflection were used to establish the purity and bond structure of WO_3 within the thin film, Selected Area Electron Diffraction gave further evidence of crystallinity within the nanostructures prepared. The potential use of the WO_3 nanoplatelet-containing thin films for hydrogen sensing at 300 °C was demonstrated.

1. Introduction

WO_3 an n-type semiconductor metal oxide with an indirect band gap of 2.7 eV is a semiconductor material that has been widely studied in the past for its electrochromic, gasochromic and conductometric properties [1–3]. It has and will continue to find use in a wide number of applications amongst which are gas sensors [4,5], smart windows [6], electrochromic devices [3,7], electrocatalysts [8], lithium-ion batteries, supercapacitors [9], etc.

It is quite well established that the manner in which materials are prepared, synthesized, and heat-treated strongly influences their particle size, crystal structures as well as their surface morphology; these in turn influence their physical and chemical properties [10–12]. A wide range of physical and chemical methods such as physical vapor deposition [13], pulsed laser deposition [14], radio frequency magnetron sputtering [5,10,15], chemical vapor deposition [8], spray pyrolysis [16], electrospinning [17,18], thermal evaporation [19], electron beam evaporation [20], electrochemical deposition [3], sol–gel 'soft chemistry' techniques [6,21], etc., have been used to synthesize WO_3 in sizes that range from bulk to nanoscale with nanostructured WO_3 in the 1, 2 and 3-dimensions being reported in several cases.

Physical methods of synthesis while being fairly controllable and suitable for producing thin films of a predetermined thickness (5 nm–3 μm) whose orientations and crystal structures are reproducible once synthesis parameters of ambient temperature, gas pressure, substrate temperature, laser fluence, vacuum conditions and target to substrate distance are determined, are however not scalable. They are also energy intensive and costly. Films produced using these methods are generally continuous, often amorphous at low substrate temperatures (25–150 °C) and are not highly ordered, if at all, in the arrangement of their crystal structure [11].

In contrast soft-chemistry solution phase methods of synthesis are known to produce at low temperatures (<100 °C) highly ordered, well-arranged, highly crystalline, continuous thin films. These methods also offer the possibility of preparing, by means of sequential deposition, multi-layered complex nanostructured films of different compositions [22], the nature of which can yield materials with added or improved functionalities and properties.

☆ The author declares that there is no conflict of interest.

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Aqueous Chemical Growth (ACG) [23] is one such solution-phase synthetic method that allows for the design of highly ordered, preferentially oriented micro/nanostructured thin films at low temperatures ($<$100 °C) [25,26]. With respect to vacuum and electrodeposition techniques the method is comparatively very cheap requiring only metal salts/precursors of the desired metal oxide to be synthesized, a regular laboratory oven, desired solid substrates, and glass bottles with screwable caps [23,27]. It is surfactant free; does not require the use of templates; is less of an environmental hazard when organics are not used, and is highly scalable allowing for the growth of thin films/coatings over large surface areas, on a wide variety of solid substrates amongst which are glass, alumina and silicon wafers [23,25,27,28].

Thin films of a large number of metal oxides have now been prepared following Vayssieres et al.'s method of Aqueous Chemical Growth, some of which are 1-D, 2-D, and 3-D nanostructures of ZnO [24], Fe_2O_3 [25], Cr_2O_3 [26], etc. Little or no work has however been reported on the synthesis of WO_3 nanostructures via the method of Aqueous Chemical Growth.

We report in this work the synthesis of WO_3 thin films by an adaptation of Vayssieres et al.'s method of Aqueous Chemical Growth. We comment on the synthesis of these nanostructured thin films of WO_3 and present results on structural characterization carried out using Scanning Electron Microscopy (SEM), Electron Dispersive X-ray Spectroscopy (EDS), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), High Resolution TEM (HRTEM), Selected Area Electron Diffraction (SAED), Fourrier Transform-Infrared Spectroscopy (FT-IR), Attenuated Total Reflection spectroscopy (ATR) and Raman Spectroscopy. The potential for hydrogen sensing of a WO_3 film produced by this method at 300 °C is also presented.

2. Experimental details

2.1. Sample preparation

Following a familiar soft-chemistry sol–gel method of preparing WO_3 [17], 3 g of Tungsten powder (99.98%) was added to a 100 mL of 30% H_2O_2 (KIMIX) while vigorously stirring in a cold bath of water, 0–15 °C. The reaction was observed to be generally exothermic and was allowed to carry on for 3–4 days during which W powder was observed to dissolve almost completely resulting in a clear, pale-yellow solution of Peroxotungstic acid (PTA) that was collected after decanting. 40 mL of the collected PTA was added to 400 mL of de-ionized water and 150 mL of iso-propanol (Merck, 99.98%). The addition of iso-propanol helps to limit the decomposition of PTA and keeps the solution stable for a long time. To this mixture of $pH = 3.1$, 65–70 mL of conc. H_2SO_4 acid (KIMIX) was added giving a solution with $pH < 0.5$. After aging for 5–7 days, 80–90 mL of the resultant solution was placed in a screw-capped Schott® glass bottle. Plain glass microscope slides (76 × 26 mm, 1 mm thick), cleaned by sequential ultrasonication in solutions of MeOH, acetone and de-ionized water for periods of 5 min each and dried with N_2, were placed in the acidified mixture of PTA, iso-propanol and de-ionized water, at an angle 70° to the horizontal. The sealed Schott® bottles were placed in an ordinary laboratory oven at 90–95 °C for 6–24 h. Upon removal a thin greenish-yellow film was observed to have deposited on the glass slides and walls of the glass bottle. A significant amount of the greenish-yellow precipitate was also observed to have been collected at the bottom of the glass bottle.

The glass slide supporting the thin film was removed from solution and heat-treatment post-deposition was carried out in two steps. This was done by drying in air at 100–150 °C for 2–3 h, then by sintering in air within a furnace at 500 °C for 2 h, at a heating and cooling rate of 50 °C/min. The greenish-yellow film initially obtained was observed to turn bright yellow post calcination.

Metal salts of W were not used in the synthesis as is the case in the synthesis of thin films of other metal oxides by ACG wherein analog metal salts of the targeted metal oxide are used. This allowed for the elimination of a washing process, the absence of which ensured that the as-deposited films were protected from disintegration when being taken out of solution. Disintegration was a result of surface tension, at the solvent–substrate interface, pulling on the surface of the deposited films during the lift-off process of the slides from the glass bottle. The use of iso-Propanol (or methanol) offered additional advantages in that these volatile solvents, with low carbon content, would evaporate rapidly from the thin films at temperatures above their boiling points of 82 °C and 65 °C respectively, leaving little or no contaminants on the surface of the films. The process of heating in air at 100–150 °C for 2–3 h assisted in burning off the organics and eliminating waters of crystallization, yielding a tungsten oxide network. Sintering at 500 °C resulted in the hardening of the metal oxide thin films, increasing their adhesion to the surfaces of the glass slides and bottle walls, and improving on the crystallinity of the films produced.

2.2. Structural characterization techniques

Knowledge of the shape, size, crystallinity and morphology of the nano/microstructures present in the thin films produced was obtained by analyzing images taken using SEM, TEM and HRTEM. SEM measurements were performed on a LEICA LEO-Stereoscan 440 digital scanning electron microscope operating at an accelerating voltage of 14–20 kV and a probe current of 50–100 pA. The LEICA scanning electron microscope was fitted with a KEVEX detector (Be window) for elemental analysis via EDS. The accelerating voltage for the electron beam used for EDS was 20 kV, with the probe current being 50 pA and the acquisition time set at 60 s. TEM was also carried out on a ZEISS LEO 912 Transmission Electron Microscope with an accelerating voltage of 200 kV, HRTEM on a FEI TECNAI G2-F20 Field Emission Gun-TEM with an accelerating voltage of 200 kV. SAED was carried out within the Transmission Electron Microscope by narrowing down the beam spot size and changing the aperture of the 200 kV high-energy electron beam. The accelerated beam was incident on the target sample such that very small sections of the sample could be examined yielding information on the crystallinity and single crystal structure of WO_3 found within the films.

X-ray Diffraction analysis for determining the crystallinity and lattice structure of WO_3 in the thin films was carried out using a BRUKER AXS D8 Advance X-ray Diffractometer (iThemba LABS) with Cu-Kα radiation of wavelength, $\lambda(K\alpha_1) = 1.5406$ Å. The X-ray tube was powered with a current of 40 mA and a voltage of 40 kV. The measurements are carried out using the Bragg–Brentano focusing technique with the X-ray tube and the detector operating in 'locked–coupled' mode. Average crystallite/grain size was calculated using the Debye–Scherrer equation after carrying out background subtraction. Crystallite size values calculated using the XRD results obtained should not be taken as absolute since the effect of instrumental line broadening on these was not taken into account.

Information about the chemical bonding in the WO_3 films was obtained using FT-IR and ATR. FT-IR spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR Spectrometer operating within the wave number range of 400–4000 cm^{-1} at a scan speed of 0.20 cm/s and a resolution of 4 cm^{-1}. The infrared spectra were obtained in ATR mode with a diamond crystal employed for the ATR measurements. A mid-infrared detector made of Deuterated Triglycine Sulphate was used in the FT-IR spectrometer. ATR was carried out within a 400–4000 cm^{-1} range using a Perkin Elmer 100 Spectrometer.

Raman Spectroscopy was carried out at room temperature in air, in the 100–1200 cm^{-1} range, this being the range in which inorganic compounds are known to have vibrational bands and metal oxides such as WO_3 are known to be active [29]. Raman was carried out with a Jobin-Yvon T64000 Raman Spectrometer coupled to an Argon ion pulsed laser as an excitation source with excitation taking place at a wavelength of 514 nm and a power of 21 mW. The beam spot