Tuning of \( \text{WO}_3 \) Phase Transformation and Structural Modification by Reactive Spray Deposition Technology

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Abstract

\( \text{WO}_3 \) nanoparticle thin films were synthesized by Reactive Spray Deposition Technology (RSDT) by varying the length of the reaction zone (9–14 cm), flow rate of quench air (0–57 L/min) and substrate temperature (80–400 °C). The resulting samples were subjected to different annealing conditions (no annealing–500 °C). Distinct metastable phases of \( \text{WO}_3 \) such as ferroelectric \( \varepsilon-\text{WO}_3 \) and the preferential orientation of the three major lattice planes \( \{002\}, \{020\} \) and \( \{200\} \) can be obtained using this synthesis technique and the morphology, and microstructure of the films are a decisive function of the synthesis process. RSDT has a strong potential to allow the properties of \( \text{WO}_3 \) to be tailored to its desired structure and application. The morphology, structure and size of \( \text{WO}_3 \) nanoparticles were probed using, X–Ray Diffraction (XRD), Raman spectroscopy, Transmission Electron Microscopy (TEM) with selected area electron diffraction (SAED), and Scanning Electron Microscopy (SEM) with X–Ray Energy Dispersive Spectroscopy (XEDS).

Keywords: \( \text{WO}_3 \) Thin Film; X–ray Diffraction; Phase Transformation; Preferential Orientation; Reactive Spray Deposition Technology

Introduction

Tungsten oxide (\( \text{WO}_3 \)) thin films have been a subject of extensive scientific investigation following the discovery of \( \text{WO}_3 \)'s gas sensing properties (\( \text{H}_2 \)[1], \( \text{H}_2\text{S} \)[2-8], \( \text{NO}_x \)[9-12], \( \text{NH}_3 \)[13-18], \( \text{O}_3 \)[19-22], \( \text{CO} \)[23-26]) and its suitability for use in breath acetone monitors as a tool for non–invasive blood glucose quantification[27-30]. The chromogenic capability of \( \text{WO}_3 \) in presence of ultra violet light, electric current[31] or gas[32] has created a whole new opportunity for the development of smart windows, optical memory, display devices, etc. Other applications include high energy density microbatteries [33,34], electro–catalysis, optoelectronics, microelectronics, and selective catalysis[35,36]. \( \text{WO}_3 \) is a semiconductor material known to exist in multiple polymorphs such as tetragonal (\( \alpha \))[37], orthorhombic (\( \beta \))[38], monoclinic (\( \varepsilon \) and \( \gamma \))[39], triclinic (\( \delta \))[40,41] and so–called pseudo cubic[42]. Each of these forms exhibits different electrical, optical and magnetic behaviors which are favorable for particular applications. For sensing functions, the \( \text{WO}_3 \) film needs to be porous and have a large surface area to enable the analytes to diffuse through the film[43]. Acentric nature and spontaneous electric dipole moment of ferroelectric \( \varepsilon-\text{WO}_3 \) leads to increased interaction with high dipole moment analytes such as acetone[44] which is used for medical devices sensing the acetone level in human breath in concentrations of parts per billion (ppb) for non–invasive blood glucose monitoring[29,45]. Photo electrochemical and photo catalytic properties are enhanced when the film is highly crystalline and preferentially oriented in the monoclinic phase because this highly crystalline structure will have fewer defects when acting as the recombination center and should suppress mu--
tual e–h+ recombination[46,47]. Polycrystalline WO3 film has almost no photochromic sensitivity whereas amorphous WO3 has high photochromic and electrochromic sensitivity due to high surface area[48,49]. However, some phases of WO3, such as ε–monoclinic is metastable at room temperature and higher temperature, thereby making it challenging to obtain such phase by the traditional synthesis processes. Here we have demonstrated a one–step flame–based direct deposition technique to engineer a particular required phase by changing the length of the reaction zone in the flame, flow rate of quench air, and the substrate temperature. RSDT is a type of flame spray pyrolysis system which is employed for synthesizing nano scale materials with high efficiency and reduced solvent waste. Here we will give a brief description of the RSDT process and, the conditions required to achieve a particular phase, and we will provide characterization results obtained by Raman spectroscopy, SEM, TEM, and XRD that prove the existence of the phases. The motivation of this research was to study the particle size, crystallinity and crystal structure of the WO3 films grown by RSDT by varying the conditions of the experiments. It is assumed that the results from this study can be used to obtain the configuration of WO3 film demanded by its application.

**Reactive Spray Deposition Technology**

Reactive Spray Deposition Technology (RSDT) was developed by Maric et al. for synthesis of nanoparticle thin films with atomic–level precision and control of properties such as phase, structure, shape, particle size distribution (0.5–100 nm), density and porosity, which can employ a broader selection of precursors compared to conventional vapor–fed flame reactors[50-66]. RSDT is a single–step, open atmosphere flame process for synthesizing nano–materials, whereby nano–particles are synthesized in the reaction zone of the flame and directly deposited on the substrate as a film or collected as particles[50-66], thereby eliminating the intermediate steps of filtration, drying, and calcination. No waste is generated because the solvent is combusted in the flame, yielding CO2 and H2O. Precise control of particle size and crystallinity can be achieved by adjusting flame setup conditions, including precursor concentration, chemistry, and flow rate; length of reaction zone; equivalence ratio (stoichiometric oxidant and fuel flow rate to actual oxidant and fuel flow rate); downstream quench air flow rate, and the substrate temperature[53]. In addition to these conditions, flame dynamics is also dependent on the solvent boiling point, enthalpy of combustion of solvent and the combustion nozzle geometry. Results from Roller, et al.[51] using RSDT, for Pt based electro–catalysts has clearly shown that the process can be adjusted to give precise control (< 1 nm) on metallic nanoparticle diameters directly deposited onto Nafion® membranes with thickness from ~100 nm to 10 μm. The reactive spray synthesis of nanoparticles relies on combustion of a solvent which also acts as a fuel and aids in the decomposition of a precursor to form nanoparticles. RSDT provides adjustable process variables such as flame temperature, stoichiometry, residence time, and downstream quenching rates that coupled with solvent and metal precursor concentrations, affect particle: nucleation, growth, annealing, and oxidation. Since the droplets produced by this process are mostly sub–micron – due to energetic inputs of heat, pressure, and supercritical propane diluent – the precursor is confined to the nanoscale regime during formation. During the particle formation process the precursor heats up, decomposes, and then undergoes a phase transition to vapor followed by concurrent reduction of the metal ions to metal or metal oxides.

**Experimental Synthesis of WO3**

An explanation of the RSDT equipment and process is described in detail by Roller, et al.[51]. Tungsten hexacarbonyl (W(CO)6) was obtained from Sigma Aldrich (Catalogue AC221040100) and was dissolved in a tetrahydrofuran (THF) (Fisher Scientific # SHBD3901V). 20 wt% sulfur free liquefied propane (Airgas catalogue # PRCP350S) was added to the above to form a precursor solution resulting in a final concentration of 5 mM/L W(CO)6, and 16.5 wt% propane. Propane assists in the atomization of the precursors by increasing the enthalpy of the solution mixture and reducing the droplet size due to supercritical expansion. The flow rate of 4 mL/min was maintained by using a syringe pump. The precursor solution was atomized by a gas–assisted external mixing nozzle (combustion nozzle) by oxygen (5 L/min). Six methane–oxygen flamelets (methane and oxygen at 0.5 L/min each) surround the capillary end, which ignites the combustible precursor mist. Prior to atomization, the precursor solution was heated to approximately 50–60 °C by enclosing the capillary by a heating coil. The precursor mist was ignited with a propane torch to obtain a bluish–white flame. At approximately 9–14 cm from the flame, a circular air quench (Exair, Super Air Wipe®) with a compressed air flow rate of 28–56 L/min at room temperature was positioned. A stainless steel substrate holder mounted on an x–y–z platform and having the option of water cooling was used for collection of WO3 particles. On the substrate holder was mounted a zero diffraction background quartz plate (MTI®) on which the film was grown. Quartz was selected for various reasons: it can withstand the high temperature required during in–situ XRD, it can be imaged in an SEM, it does not have an interfering background in a Raman spectrometer, and the film can be scraped off for TEM analysis.

![Figure 1. The setup of Reactive Spray Deposition Technology (RSDT)](image)
Role of air quench

A schematic of the air quench is shown in figure 2. The air quench is a circular ring with an internal annular chamber. The compressed air at room temperature enters the two nozzles and is directed towards that chamber. The chamber has a narrow ring nozzle through which the air adopts the coanda profile and flows along the angled surface of the air quench. This also creates a low pressure region behind the air quench causing the entrainment of the surrounding air into the primary air stream. A 360˚ cone of cold air is formed which cools the nanoparticles instantly and prevents growth, agglomeration, and sintering, thereby keeping the particle size small and increasing the active surface area. The distance between the combustion nozzle and the air quench is considered the reaction zone and the length of the reaction zone is proportional to the residence time of the nano–particles in the zone. Adjusting the length of the reaction zone and the flow rate of compressed air gives unique conditions to obtain an assortment of phases and structures of WO₃.

Characterization

In–situ X–ray diffraction patterns of WO₃ film were recorded in air at 30 ˚C, 150 ˚C, 250 ˚C, 300 ˚C, 350 ˚C, 400 ˚C and 500 ˚C on a Bruker D8 advanced powder diffractometer using CuKα radiation. Heating rate of 5 ˚C /min was used with a hold time of 1 hr at the temperature of the scan. Crystallite size was measured by using Debye Scherrer method. Raman spectra were obtained with a Renishaw Ramascope micro–Raman spectrometer fitted with a reflected light microscope using a 50 mW laser (514.5 nm) and exposure time of 30 s at ambient conditions. Instrument alignment was optimized using a 519 cm⁻¹ signal of a silicon wafer. Raman measurements were performed since this technique is well known to give the “fingerprint” of WO₃ material[67].

Results and Discussion

X–ray diffraction

γ and ε WO₃ with different phase ratio was synthesized in four different set of conditions in RSDT as described in table 1 by altering the length of the reaction zone, flow rate of quench air and temperature of substrate. Figure 3 shows the X–ray diffraction spectra for the samples A, B, C and D. It is clear from the figure that very different structures of WO₃ were obtained by changing the conditions of the flame. All four samples were monoclinic, the most dominant structure of WO₃ and which can be indexed to ICDD#00–043–1035 (space group P2₁/n). Sample A is the as–prepared sample with no post annealing, and it shows a well crystalline structure with (002) preferential plane oriented at 2θ = 23.1 ˚. This could be due to the high temperature of the particles in the absence of quench air which can cause the migration of WO₃ atoms towards the lower energy nucleation sites[68].

All the other samples (with the exception of A) were found to be amorphous in nature because the quench was close to the nucleation site. This amorphous structure could arise because the particles are air quenched as soon as they are produced from the flame and the temperature of the particles and substrate did not exceed 200 ˚C. The amorphous samples were thermally annealed in the high temperature stage of the XRD—the crystallization steps and the corresponding XRD patterns can be found in the supplementary information. Thermal annealing of amorphous WO₃ causes the particles to become crystalline and it also changes the phase ration, grain size, porosity, density of adsorption sites and pore volume[43]. It is clear from in–situ XRD that the crystallization of the WO₃ particles started at 350 ˚C. Sample B was prepared with no air quench; however the substrate temperature was maintained at 200 ˚C by the water cooled substrate holder and the sample thereby retained an amorphous structure. By comparing the XRD spectra of sample B with that of Wang, et al. [29] and Righter-
toni, et al. [45] it can be concluded that the sample is mostly ε–WO₃, the metastable phase at room temperature. Sample C is oriented preferentially along the (200) direction. This preferentially-oriented crystallization was also observed by Sun, et al. [69] and Zhifu, et al. [43] who prepared their films by physical vapor deposition (PVD). Sun et al. suggested that preferential orientation along the (200) direction happened to reduce the lattice mismatch with the sapphire lattice on which the film was grown. According to Zhifu, et al. the cause of this behavior was the column–like accumulation of the WO₃ species during the sputtering process at the operating pressure 20 Pa. The (200) orientation could also form in–situ during the annealing process. Sample D is oriented along the (020) plane direction, and sample A is oriented along the (002) direction, as was also reported by Garavand, et al. [70] Guo, et al. [71] and Jing, et al. [46]. Guo, et al. evaluated the photoelectrochemical activity and photoconversion efficiency of self–assembled nanoporous WO₃ and WO₃ film with preferential orientations at (002) and (020), respectively. They found that the photocurrent of the (002) plane–oriented WO₃ was 9 times the value and the photoconversion efficiency was 4.57 times higher than those of (020) plane–oriented WO₃. Furthermore, (002) WO₃ was more favorable in absorption and redox of pollutants than (020) WO₃. Jing, et al. found that the (002) preferential orientation of WO₃ resulted in higher photocatalytic degradation of NO[46].

The spectra are similar to those of the monoclinic WO₃ as apparent from the strong peaks at 808 and 715 cm⁻¹. The peak at 450 cm⁻¹ can be assigned to the quartz substrate as determined by the scan of quartz substrate without any film. The intensity of the substrate peak is different for the samples because of the difference in the thickness of the film. A relatively strong peak is obtained at below 150 cm⁻¹ for all the samples which can indicate the O–O deformation mode[72]. Salje et al. has obtained the Raman spectra of the monoclinic (γ and ε) WO₃ and is reported in reference[72],[73]. After comparing with Salje, et al. it can be assumed that the peaks at 205, 310, 372, 394, 427, 645, 680, 697cm⁻¹ can be assigned to ferroelectric ε–WO₃ while peaks at 327, and 716 cm⁻¹ are for γ–WO₃ only. There is clearly an overlap between γ and ε WO₃ as evident from the spectra.

Table 1. Synthesis conditions of WO₃ in Reactive Spray Deposition Technology

| Sample | Substrate temperature (°C) | Quench air flow rate (L/min) | Length of reaction zone (nozzle to substrate) (cm) | Preferential plane orientation | Crystallite size (nm) |
|--------|-----------------------------|-----------------------------|-----------------------------------------------|-----------------------------|---------------------|
| A      | 350-400                     | 0                           | 17.1                                         | 002                         | 33.1                |
| B      | 200                         | 0                           | 13.3                                         | NONE                        | 61.6                |
| C      | 100-130                     | 28.3                        | 20.6                                         | 200                         | 29.0                |
| D      | 80                          | 56.6                        | 12.6                                         | 020                         | 42.3                |

Figure 4. Raman spectroscopy for samples A, B, C, and D showing mostly monoclinic structure.

Figure 4 shows the Raman scattering measurements of untreated sample A and the post–annealed samples B, C and D (since the Raman signal of WO₃ cannot be obtained for amorphous structure).

Figure 5. Scanning Electron Microscopy micrographs of WO₃ films deposited by RSDT under condition A, B, C and D. (Top: as deposited, Bottom: after annealing at 500 °C)

Electron Microscopy

Scanning Electron Microscopy

Figure 5 shows the SEM micrographs of the WO₃ film as deposited (top) and after annealing at 500 °C. Films A and D are very homogeneous while B and C shows particle agglomeration. As is clear from the figure, the size of the grains are in the order B=D>A>C. Pores and cracks can be seen in
samples A and D while samples B and C show uniform morphology. It is interesting to see that in samples A and D, the pores and cracks have grown in size after annealing at 500 °C. This same phenomenon was observed by Santato, et al. and could be due to the elimination of organics from the film surface after heat treatment[74]. Increase in porosity of the films is advantageous to the sensing function of WO₃ since this favors diffusion of analytes in the bulk of the film. The images indicate high quality of WO₃ films deposited by RSDT.

**Transmission Electron Microscopy**

Figure 6 shows the bright field TEM micrographs along with the SAED pattern of samples A–D after post annealing. All samples were polycrystalline, as evident from the SAED pattern and were indexed to monoclinic WO₃. As measured from the micrographs the size of the WO₃ particles were 15–40 nm for sample A, 30–50 nm for sample B, 20–25 nm for sample C, and 20–30 nm for sample D. Different shapes and sizes of particles were seen from the micrographs, as labelled. Sample A shows faceted particles with edges and corners. Samples B and D show circular particles, whereas circular, oval, elliptical, and dumb bell shaped particles can be seen in sample D. Only sample B depicts the formation of necks between individual WO₃ particles.

**Conclusions**

Reactive Spray Deposition Technology was employed to synthesize WO₃ (γ and ε phase) thin films of from the vapor phase. The morphology, structure and preferential lattice plane orientation was tuned by changing the parameters of the flame set-up including substrate temperature, quench air flow rate and length of reaction zone. It was determined that the particular structure and properties of WO₃ are a function of the synthesis process. By employing the RSDT, the properties of WO₃ can be tuned to be favorable towards a particular application. Our next publication will elaborate upon this technique for exploring the sensing function of WO₃ by changing the synthesis conditions.

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