



Characterization of Nb-doped WO₃ thin films produced by Electrostatic Spray Deposition

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ABSTRACT

In this paper we provide full characterization of Nb-doped WO₃ thin films produced by Electrostatic Spray Deposition on glass substrates. The films were produced by electro spraying a tungsten isopropoxide in 2-propanol precursor solution in a temperature-controlled environment. Film morphologies and crystal structures were characterized by Scanning Electron Microscopy, Transmission Electron Microscopy, and X-Ray Diffraction, whereas band gap values, composition, and oxidation state of the materials were determined by Ultraviolet-Visible Spectroscopy, Energy Dispersive X-Ray, and X-Ray Photoemission Spectroscopy, respectively. It is shown that highly-porous tree-like morphologies can be achieved by adjusting the deposition temperature to 325 °C. Under these conditions, the size of the primary particles of the films ranges from 150 to 200 nm, and their crystallinity can be varied from completely amorphous for the as-deposited samples to hexagonal structures for the annealed samples. The measured Nb content of the doped samples was found to be similar to that of the precursor solution, leading to an increase of the band gap of 0.23 eV as compared to the pure WO₃ samples.

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1. Introduction

Metal Oxide Semiconductor (MOS) nanostructured thin films find many applications in gas sensing [1], energy storage [2], and catalysis [3]. Such films can be produced by a wide number of methods including pulsed laser deposition (PLD) [4], radio frequency magnetron sputtering [5], hydrothermal synthesis [6] or aerosol-based techniques [7]. The latter have many advantages for synthesizing particle building blocks of well-defined size, morphology, and composition [8], thereby enabling the fabrication of nanostructured materials with good control over their structure [9].

A simple and cost-effective method for fabricating nanostructured thin films using aerosol-based techniques is by combining electrohydrodynamic atomization with electrostatic deposition, called Electrostatic Spray Deposition (ESD) in short. In order to synthesize the nanostructured thin films by ESD, a high voltage difference (several kilovolts) is applied between a metallic nozzle and a counter electrode (i.e., the substrate). When feeding the nozzle with a precursor solution, the liquid at the end of the nozzle is atomized into micron-sized

droplets by means of electrostatic forces. Due to the strong electric field, the highly charged droplets are then driven to the substrate which is heated to enhance the evaporation of the solvent and to partially oxidize the deposited material.

The ESD technique has been used for the synthesis of a wide range of metal oxide nanomaterials for applications in Li-ion batteries [10], in solid oxide fuel cells [11,12], in coatings [13], and in sensors [14]. With respect to the latter application, thin films of SnO₂, ZnO, or WO₃ have been widely used in solid-state gas sensors because of their low cost, simplicity, and good sensitivity [15]. WO₃ thin films in particular have been used for measuring the concentration of NH₃, NO_x, SO₂, CH₄, and H₂, in the range from 1 to 1000 ppm [16]. To measure concentrations down to ppb levels, however, their sensitivity needs to be improved. This can be achieved by a number of ways such as increasing the porosity of the thin film, or creating active sites at the surface of the film by doping with metals (e.g., Pd, Pt, Au), or by using combinations of MOS, e.g., WO₃-SnO₂ or WO₃-TiO₂ [17,18].

In the present study we investigate the properties of nanostructured Nb-doped WO₃ thin films produced by ESD in view of enhancing their properties for use in gas sensors. The morphology and crystal structure of the samples are characterized by imaging techniques, i.e., Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and by X-ray Diffraction (XRD). The band gap, the composition, and the oxidation state of the materials are determined by Ultraviolet-

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Visible (UV–Vis) spectroscopy, Energy Dispersive X-Ray spectroscopy (EDX), and X-Ray Photoelectron Spectroscopy (XPS), respectively.

2. Materials and methods

In order to synthesize thin films of tungsten-based materials by ESD, we prepared precursor solutions by mixing tungsten isopropoxide ($W(i_{Pr})_6$, 5% w/v in 2-propanol, Alfa Aesar) with dopant precursors at a W/dopant atomic ratio of 5. More specifically, 5 mL of $W(i_{Pr})_6$ were mixed with 50 mL of 2-propanol in a bottle under an argon atmosphere. Niobium chloride ($NbCl_5$, 99.9% purity, Sigma-Aldrich), was then added in a 5:1 atomic ratio and stirred for 1 h. The as-prepared precursor solutions were then introduced into a 5-mL glass syringe (Fortuna Optima) and pumped through a 25-mm long nozzle (Nordson EFD; inner diameter of 0.25 mm and outer diameter of 0.52 mm).

The flow rate of the precursor solution through the nozzle was set to 0.2 mL/h, whereas the applied voltage between the nozzle and the substrate (counter electrode) ranged from 6 to 9 kV depending on the conductivity of the solutions. The particles were deposited for 1 h on 0.40-mm thick and 18-mm wide square glass substrates. Initially we performed tests to investigate the influence of temperature on the morphology of the materials (cf. Section 3.1), where the optimal temperature of the system was found to be 325 °C. After deposition, the films were annealed at 550 °C for 6 h in order to remove the last traces of solvent that could remain within the layer, and to stabilize the thin film structure.

For the characterization of the size of the particles and the morphology of the thin films, we used an SEM (Philips XL20) operated at 15 kV. To avoid any surface charge disturbances during the SEM measurements, the samples were coated with a thin film of gold by sputtering. To investigate further the effect of annealing on the crystallinity of the building blocks of our structures we collected particles from the as-deposited and annealed films and observed them under a TEM (FEI TECNAI TF20). These samples were prepared by collecting particles from the films and dispersing them into 99.9% pure ethanol. Droplets of the ethanol solutions were then spread on a carbon-polymer layer supported on a copper grid (Quantifoil® microgrid), and the solvent (i.e., the ethanol) was allowed to evaporate at room temperature. The grid was then introduced in the TEM that was operated at 200 kV.

The evolution of the sample structures after annealing was studied by XRD (Bruker AXS D8 Advance) with a $Co K\alpha$ radiation source ($\lambda = 1.78897 \text{ \AA}$). X-Ray Diffraction patterns were measured in the 2θ angles ranging from 5 to 90° both for as-deposited samples and samples after annealing at 400 and 550 °C for 6 h. In order to determine the oxidation state of the elements introduced within the films, we employed an X-Ray photoemission spectrometer (PHI 5400 ESCA) that employed a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV ion-gun. The input lens to the analyzer was set at a take-off angle of 45° with respect to the normal of the sample surface. The input lens aperture used was $3.5 \times 1.0 \text{ mm}$. All spectra were recorded using unmonochromatized $Al-K\alpha$ (1486.6 eV) radiation. The X-ray source was operated at an acceleration voltage of 13 kV and at a power of 200 W. During the spectrum acquisition the background pressure of the ultrahigh vacuum system was $5 \times 10^{-7} \text{ Pa}$ or less. Full spectra between 0 and 1000 eV using 0.5 eV step size and pass energy of 89.45 eV were recorded before performing the more localized measurements. To investigate the band gap changes of the samples, optical transmissions were recorded in the UV–Vis and near Infrared range by a Perkin-Elmer Lambda 900 spectrophotometer equipped with an integrated sphere (Labsphere). Depending on the sample's position within the sphere (in front, within, or behind the sphere), spectra of transmitted and reflected radiation having wavelengths from 200 to 2400 nm were obtained. To evaluate the band gap of the films using the UV–Vis measurements, we also need to have information on the thickness of the samples. This was estimated using a profilometer (Dektak 8) with an applied force of 0.03 N on the sample surface.

3. Results and discussion

3.1. Scanning Electron Microscopy

Fig. 1 shows images of the structures of the thin films obtained by varying the temperature of the substrate from 250 to 400 °C. Substrates at lower temperatures (i.e., of the order of 250 °C) lead to a dense morphology, evolving to grain-like structure at 275 °C, and more porous tree-like morphologies when the substrate temperature increases to 300 °C and 400 °C. When the temperature of the substrate rises above 350 °C, however, the adhesion of the film to the glass substrate is reduced drastically. As a result, the synthesis temperature was selected to be 325 °C in order to achieve high porosity and good adhesion of the film to the substrate.

Similar structures of WO_3 thin films prepared by ESD using tungsten ethoxide as the tungsten precursor have been observed by Ghimbeu et al. [19]. In our case, however, the use of a multijet spraying mode, as discussed in Section 3.2 below, resulted in structures of higher porosity. The WO_3 layers we produced are composed of primary particles having diameters ranging from around 1 μm for samples prepared at temperatures lower than 300 °C, to 200 nm and lower for higher temperatures. Samples prepared at temperatures above 300 °C that lead to a tree-like morphology consist of particle aggregates having an average size between 10 and 20 μm .

High porosity is one of the most important requirements for MOS nanostructures used as gas sensors as morphologies with high surface-to-volume ratio increase the interaction between the film and the target gas, thereby enhancing the sensor's sensitivity and response time. Porosity also strongly affects gas diffusion through the pores of the thin film, whether it is by molecular diffusion (for pore sizes $> 100 \text{ nm}$) or Knudsen diffusion (pore sizes $< 100 \text{ nm}$). It has also been noticed that for some MOS sensors, porosity could also influence the selectivity and can play a more important role than the particle size [20]. The high porosity obtained with ESD as operated in our work can be advantageous for gas detection, as it increases the samples' active surface for adsorption of the target gas. Yet, because of the high charge density of the deposited particles, the films exhibit poor contacts and grain boundaries between the tree units that could disturb the transmission of an electrical signal during sensing measurements as a result of the high charge density of the deposited particles.

Similar structures with those using undoped WO_3 were observed with Nb-doped samples (cf. Fig. 2). The only difference was that the doped samples exhibited smaller aggregates (1 to 5 μm) compared to the undoped films (10 to 20 μm). The introduction of dopants in the materials produces smaller particle sizes and increases the lattice strains, which in turn reduces grain growth during annealing as has been shown by Fend et al. [21].

3.2. Evaluation of droplet sizes and particle sizes

Two modes of jet break up can be distinguished while spraying according to the electrohydrodynamic atomization model developed by Hartman [22]: the varicose mode in which the jet breaks up into larger primary and smaller secondary droplets, and the whipping mode in which the jet is elongated and laterally displaced before the break up point. In the varicose mode, which is used in this work, the size of the droplets immediately after the jet breakup can be estimated by [22]:

$$d_{d,v} \approx \left(\frac{16\rho\varepsilon_0 Q^3}{\gamma K} \right)^{\frac{1}{6}}, \quad (1)$$

where ε_0 is the permittivity of vacuum ($8.85 \times 10^{-12} \text{ A}^2 \cdot \text{s}^4 \cdot \text{kg}^{-1} \cdot \text{m}^{-3}$), Q is the solution flow rate (in mL/h), K is the electrical conductivity (see Table 1 for measured values in $\mu\text{S} \cdot \text{cm}^{-1}$), γ is the surface tension of

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