CrystEngComm

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Connectivity enhancement of highly porous WO_3 nanostructured thin films by in-situ growth of $K_{0.33}WO_3$ nanowires

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Julien Gaury,[a] Ugo Lafont,[b] Eugene Bychkov,[c] Andreas Schmidt-Ott,[a] and George Biskos [a, d]

Electronic Supplementary Information (ESI)

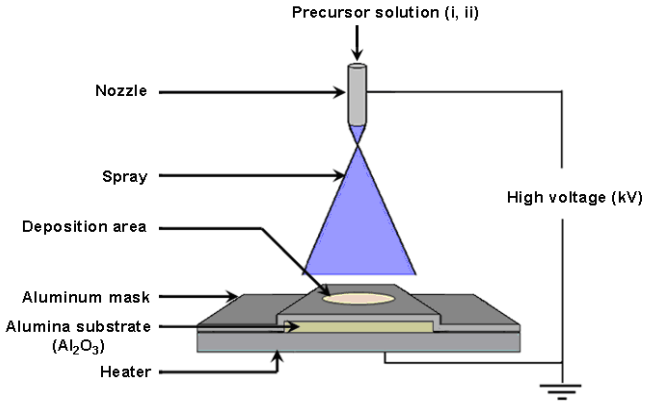
Experimental

Thin film deposition:

The electrostatic spray deposition setup that we used to produce the WO_3 thin films has been described elsewhere.[1] In short, a precursor solution was prepared by diluting 5 mL of tungsten isopropoxide ($W(^{i}_{Pr})_6$, 5% w/v in 2-propanol, Alfa Aesar) in 45 mL of 2-propanol and pushed through a 25-mm long metallic nozzle (ID = 0.25 mm and OD = 0.52 mm) at a flow rate of 0.4 mL h^{-1} using a syringe pump. A high potential difference (9 - 12 kV) was applied between the nozzle and an opposed counter electrode in order to charge the solution and to induce the break-up of the liquid jet into spray droplets (ESI Fig 1). The generated droplets were driven by electrostatic forces to the counter electrode which was located 20 mm from the tip of the nozzle and heated to 350 °C to induce evaporation of the droplets.
Alumina substrates (Gimex Technische Keramiek, 99 % Al_2O_3, 10× 20×0.381 mm) having two Pt electrodes were placed on the heated counter electrode. To focus the deposited particles in the region between the two Pt electrodes we used an aluminum foil with a 10-mm hole on top of the alumina substrates. The total volume of the precursor solution sprayed for each sample was 1.2 mL.

Potassium post-conditioning:

The post-conditioning with potassium was carried out immediately after the WO_3 deposition. For that, we used the ESD setup to spray potassium-containing solutions on the as-deposited WO_3 thin films at room temperature. The post-conditioning was conducted for 10 minutes using a flow rate of 0.6 mL h^{-1}. A 10 kV potential difference was used between the nozzle and the counter electrode, and the resulting droplet was charged neutralized in order to improve the homogeneity of the potassium coverage onto the as-deposited WO_3 layer.



ESI Fig. 1. Electrostatic Spray Deposition (ESD) setup, illustrating the two-step process for the fabrication of the nanowires by: (i) Deposition of the WO_3 tree-like nanostructures and (ii) Post-conditioning of the pre-deposited layer with a potassium-containing solution.

Annealing procedure:

After the potassium deposition, the samples were placed in an oven (Nabertherm, model S27) under open atmosphere and heated to 500 °C. The samples were inserted inside the furnace before heating and the temperature was increased from ambient to 500 °C at a rate of 2 °C min^{-1}. The temperature was then maintained at 500 °C for 20 hours (for the films used in the resistance measurements shown in Fig. 3 we used annealing times of up to 40 hours) before being turned off and slowly cooled to room temperature.

Equipment:

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 measurements, the samples were coated with a thin film of gold by sputtering. Transmission Electron Microscopy was performed with a FEI TECNAI TF20, operated at 200 kV. The samples were prepared by collecting particles from the films that were then dispersed into ethanol (99.9% purity). Droplets of the ethanol solutions were 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.

Resistance measurements were performed on pure and KOH-conditioned WO_3 samples deposited onto Al_2O_3 substrates with Pt electrodes. The electrodes were then connected to a Keithley 6517A electrometer to measure the electrical resistance of the samples at room temperature, using a bias voltage of 10 V.

Notes and references

[a] Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628BL Delft, The Netherlands.
[b] Aerospace Engineering, Delft University of Technology, Kluyver 1, 2629HS Delft, The Netherlands.
[c] Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Cote d'Opale, 189A Avenue Maurice Schumann, 59140 Dunkerque, France.
[d] Department of Environment, University of the Aegean, University Hill, 81100 Mytilene, Greece.

1 J. Gaury, E. M. Kelder, E. Bychkov, G. Biskos, *Thin Solid Films*, 2013, 534, 32.