Sensors and Actuators B 147 (2010) 453–460

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

# Growth of $SnO_2/W_{18}O_{49}$ nanowire hierarchical heterostructure and their application as chemical sensor

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ARTICLE INFO

*Article history:*
Received 30 October 2009
Received in revised form 6 April 2010
Accepted 12 April 2010
Available online 18 April 2010

*Keywords:*
Nanowires
Hierarchical heterostructure
Hetero-junction
Sensors
Intragrain
Grain-boundary

ABSTRACT

Hierarchical heterostructures consisting of $W_{18}O_{49}$ nanowires grown on $SnO_2$ nanowires have been prepared by sequential thermal evaporation of tin and tungsten under partial oxygen atmosphere. Sensors made using isolated heterostructure nanowires showed superior selectivity for the detection of chlorine in comparison to isolated pure $SnO_2$ nanowires as well as mat type films prepared using heterostructure nanowires. Improved response compared to mat type films arises due to different sensing mechanisms of chlorine arising from its adsorption or replacement of oxygen. On the other hand better selectivity in comparison to isolated $SnO_2$ nanowires has been attributed to transfer of electrons across hetero-junction from $W_{18}O_{49}$ to $SnO_2$ and lower sensitivity of $W_{18}O_{49}$ to $H_2S$. The results show potential of tailored hierarchical nanoheterostructures for the fabrication of gas sensors.



## 1. Introduction

Metal oxide semiconductors are versatile materials due to their diverse properties and functionalities. Bulk properties such as piezoelectricity, chemical sensing, and photoconductivity of these materials are enhanced in their Quasi one-dimensional (Q1D) form. Interestingly, Q1D structures can be used as template for the growth of other nanostructures resulting in novel hierarchical nanoheterostructures with enhanced functionality.

Growth of various nanowire heterostructures has been reported for different potential applications [1–4]. Heterostructures with p-type Si core and n-type CdS shell were synthesized [1a] by pulsed laser deposition of CdS on Si nanowires and used for the fabrication of light emitting diodes (LED). ZnO tetrapods covered with $SnO_2$ shells [1b] showed improved luminescence properties. Nanoheterostructures, consisting of $In_2O_3$ cores and ZnO nanowires grown on them, have been prepared in single step by heating $In_2O_3$, ZnO and graphite [2a]. ZnO nanorods have been grown on carbon nanotubes (CNT) and GaN nanowires [2b] for fabrication of LED devices. While many nanoheterostructures have been shown to have potential for applications, very few actual applications have been demonstrated. In very few studies, potential of nanoheterostructures for gas sensing has been reported. Chen et al. [5] have shown good sensitivity of thin films of $SnO_2/\alpha$-$Fe_2O_3$ heterostructures to ethanol (0–500 ppm range) at operating temperatures between 250 °C and 350 °C. Similarly, Zhua et al. [6] have prepared heterostructures consisting of $\alpha$-$Fe_2O_3$ cores and ZnO shells. Films of these heterostructure also showed good sensitivity to ethanol at 220 °C. Clearly there is a need to carry out further studies in this area. In this paper, we report the preparation of $SnO_2$:$W_{18}O_{49}$ hierarchical heterostructures and their application as selective chlorine sensors operating at room temperature. Heterostructures of $SnO_2$:$W_{18}O_{49}$ have been selected for study as $SnO_2$ is one of the most important material for gas sensing applications [7] and oxides of tungsten including $WO_3$ and $W_{18}O_{49}$ have shown promise for the detection of gases [8].

Nanostructured materials have been of interest for gas sensing applications due to two reasons. Firstly, due to increased surface area and defect structure these have higher reactivity leading to better sensor characteristics. Secondly, it is possible to fabricate miniature sensors using individual Q1D structures [9]. Two different kind of sensors based on 1D structures have been reported: (a)

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doi:10.1016/j.snb.2010.04.016

films of nanostructured materials typically prepared by putting few drops of suspension of material in organic solvent on an insulating substrate and (b) isolated nanowire sensors prepared using techniques such as focused ion beam (FIB) [10] and dielectrophoresis [11].

Sensors based on nanostructured films have been reported using different oxide materials. In a study by Wan et al. [12], ZnO nanowire films were reported to show good sensitivity to ethanol in 1–200 ppm range at operating temperature of 300 °C. Mats of randomly oriented $SnO_2$ nanowires [13] showed good sensitivity to 2-propanol at operating temperature of 300 °C. Tungsten oxide nanowire network has been reported for the detection of $H_2S$ and $NO_2$ (50 ppb concentration) gases [8a,14] and films of $In_2O_3$ nanowires showed sensitivity to $NO_2$ in ppb range [15]. Bundles of $W_{18}O_{49}$ nanowires have been reported to show sensitivity to ppb level of ammonia at room temperature [8b]. In a review article, hierarchical and hollow nanostructures have been shown to be very promising for gas sensor applications [16]. Some of the isolated nanowire sensors reported in the literature are (a) ZnO nanowire sensors fabricated using FIB/SEM with high sensitivity to hydrogen at 10 ppm concentration [10] and (b) $SnO_2$ nanowires having good sensitivity to hydrogen [17].

In the present study, hierarchical heterostructures consisting of small $W_{18}O_{49}$ nanowires grown on larger $SnO_2$ nanowires have been prepared resulting in heterostructure nanowires (HSNW). These HSNW have been employed for preparation of isolated HSNW sensors as well as mat type film sensors. The results have been compared with similar pure $SnO_2$ nanowire sensors. This is possibly the first study where advantage of nanoheterostructures for room temperature detection of a gas has been shown and isolated NWHS have been used for sensing of gases. The study shows that tailored nanoheterostructures may yield gas sensors with improved characteristics.

## 2. Experimental

The growth of $SnO_2$:$W_{18}O_{49}$ hierarchical heterostructures was carried out in two steps. In the first step, $SnO_2$ nanowires (mixed with nanobelts) were grown by thermal evaporation of Sn in a horizontal tubular furnace. Sn powder (99.99% pure) was loaded in an alumina boat and was placed at the centre of a quartz tube. Temperature of the boat was raised to 900 °C at a rate of 300 °C/h in the presence of Ar and 1% $O_2$ gas flow. The growth was carried out for 1 h at 900 °C. It may be noted that the melting point of Sn is 232 °C, but it needs temperature of 997 °C to attain a vapor pressure of $10^{-4}$ mbar, while tin oxide (melting point 1127 °C) sublimes with a vapor pressure of $10^{-4}$ mbar at 350 °C. Therefore, the evaporation of Sn occurs after its oxidation. After growth, the furnace was cooled to room temperature at a rate of 300 °C/h. $SnO_2$ nanowires were deposited on upper side walls of the alumina boat [18]. In the second step, tungsten oxide nanowires were grown on $SnO_2$ nanowires by thermal evaporation of tungsten in a vacuum deposition system in the presence of air at a pressure of $2.5 \times 10^{-4}$ mbar [19]. A collection of $SnO_2$ nanowires was placed at a distance of 2 cm from tungsten filament and the system was evacuated to $2 \times 10^{-5}$ mbar. The depositions were carried out for 30 min at a source temperature of ~1965 °C. The temperature of the filament was measured using a pyrometer (RAYTEK make). The pressure inside the chamber was maintained by controlled flow of air through a needle valve. The deposition occurs by slow oxidation of tungsten filament followed by evaporation, as oxides of tungsten are volatile. For example, a vapor pressure of $10^{-4}$ mbar occurs at 980 °C for $WO_3$ compared to 2760 °C for tungsten metal (melting point of tungsten is 3422 °C and that of $WO_3$ is 1473 °C). The substrates with $SnO_2$ nanowires were not intentionally heated but during deposition their temperature increased to 700 °C. A uniform blue deposit was observed on the $SnO_2$ nanowires after the deposition. No metal catalyst was used during the synthesis of the heterostructures and their growth is attributed to vapor solid mechanism. To study effect of growth parameters, the depositions of $W_{18}O_{49}$ were also carried out at different filament temperatures between 1850 °C and 2050 °C and at pressures between $5 \times 10^{-5}$ mbar and $7 \times 10^{-4}$ mbar. For comparison, $W_{18}O_{49}$ was also deposited on bare alumina substrates in a manner similar to the growth of nanowires. In this case, growth of thin films instead of nanowires was observed.

Morphology of the samples was investigated using scanning electron microscopy (SEM) (TESCAN make VEGA MV2300T/40 system) and transmission electron microscopy (TEM) (JEOL 2000 FX) techniques. The crystalline nature and phase formation were studied by grazing angle X-ray diffraction (XRD) measurements. The chemical state of the hierarchical nanostructures were determined by X-ray photoelectron spectroscopy (XPS) analysis carried out using Al Kα (1486.6 eV) radiation (XPS system consisting of X-ray source Model CX700 and MAC-2 electron analyzer). The Raman spectra were recorded at room temperature using 532 nm line from a diode pumped $Nd^{3+}$:YAG laser (SUWTECH laser, model G-SLM-020 from Shanghai Uniwave Technology Co. Ltd.) operated at a power of 15 mW. Emitted light was collected in back-scattered geometry and detected using 0.9 m monochromator and cooled CCD (Andor Technology) detector with entrance slit width of 50 μm.

Two different types of sensors (mat type and isolated HSNW type) were fabricated using heterostructures. For preparation of mat type (film) sensors, two gold electrodes were deposited on alumina substrates by thermal evaporation. Heterostructure nanowires were dispersed in ethanol and then coated on alumina substrates to yield a film of heterostructures. Resistance of the film between two gold electrodes was measured to study response to gases. Isolated heterostructure nanowire (also called single HSNW) sensors were fabricated by dispersing very small quantity of heterostructures in ethanol and placing a drop of this dilute suspension on a glass slide. Single HSNW were separated using optical microscope (visibility under optical microscope was improved by some ethanol sticking to heterostructures by surface tension) and a metal mask was aligned on isolated nanowires for deposition of two gold electrodes with 12 μm spacing (12 μm metal wire was used for this purpose). Gold deposition was carried out by thermal evaporation technique. Response of sensors to various gases was measured using a system described earlier [20]. Briefly, sensors were placed in a 250 ml container and measured quantity of gas was injected using a syringe so as to yield the desired concentration of gas in the container. Current through nanowires was measured (under different atmospheres) for a constant voltage applied across the gold pads using Kiethley picoammeter (model 6487 picoammeter/voltage source). The response was calculated as $S = I_g/I_a$; where, $I_g$ is the current in the presence of gas and $I_a$ is the current in air. The response and recovery times were also determined on exposure to gases. For this purpose, response time is defined as the time taken to attain 90% of the maximum change in conductance on exposure to gas and the recovery time is the time taken to recover to within 10% of the base conductance after removal of gas. For comparison, response was also measured on sensors made using single nanowires and mat type films of $SnO_2$ (prepared in a manner similar to corresponding heterostructure sensors).

## 3. Results and discussion

SEM micrographs of $SnO_2$ nanowires/nanobelts and heterostructures (prepared at source temperature of 1965 °C and air