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

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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 SnO₂ 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

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 heterojunction 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.

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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/α -Fe₂O₃ 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 α -Fe₂O₃ 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 SnO₂:W₁₈O₄₉ hierarchical heterostructures and their application as selective chlorine sensors operating at room temperature. Heterostructures of SnO₂:W₁₈O₄₉ have been selected for study as SnO₂ 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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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 SnO₂ 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 H₂S and NO₂ (50 ppb concentration) gases [8a,14] and films of In_2O_3 nanowires showed sensitivity to NO₂ in ppb range [15]. Bundles of W₁₈O₄₉ 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) SnO₂ 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 SnO₂:W₁₈O₄₉ hierarchical heterostructures was carried out in two steps. In the first step, SnO₂ 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% O₂ 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. SnO₂ nanowires were deposited on upper side walls of the alumina boat [18]. In the second step, tungsten oxide nanowires were grown on SnO₂ nanowires by thermal evaporation of tungsten in a vacuum deposition system in the presence of air at a pressure of 2.5×10^{-4} mbar [19]. A collection of SnO₂ nanowires was placed at a distance of 2 cm from tungsten filament and the system was evacuated to 2×10^{-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 WO₃ compared to 2760 °C for tungsten metal (melting point of tungsten is $3422 \,^{\circ}$ C and that of WO₃ is $1473 \,^{\circ}$ C). The substrates with SnO₂ nanowires were not intentionally heated

but during deposition their temperature increased to 700 °C. A uniform blue deposit was observed on the SnO₂ 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 W₁₈O₄₉ were also carried out at different filament temperatures between 1850 °C and 2050 °C and at pressures between 5×10^{-5} mbar and 7×10^{-4} mbar. For comparison, W₁₈O₄₉ 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 Ka (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 Nd³⁺: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 $12 \,\mu m$ spacing ($12 \,\mu m$ 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 SnO₂ (prepared in a manner similar to corresponding heterostructure sensors).

3. Results and discussion

SEM micrographs of SnO₂ nanowires/nanobelts and heterostructures (prepared at source temperature of 1965 °C and air



Fig. 1. SEM images of (a) pure SnO₂ nanowires, (b-c) SnO₂:W₁₈O₄₉ heterostructure nanowires at low and high magnification and (d) highly magnified image of W₁₈O₄₉ nanowires.

pressure of 2.5×10^{-4} mbar) are shown in Fig. 1. SnO₂ nanowires were found to have diameter in 70–300 nm range and length in 5–100 μ m range (Fig. 1a). In heterostructures, a dense growth of tungsten oxide nanowires with ~50 nm diameter and more than 2 μ m length was observed on SnO₂ nanowires.

Typical XRD spectrum of heterostructures (Fig. 2) showed presence of SnO₂ (rutile phase with *a*=4.74 and *c*=3.1885 Å) and monoclinic W₁₈O₄₉ phases (with *a*=18.33, *b*=3.786, *c*=14.04 Å) [19]. No mixed or impurity phases were detected indicating heterostructures with pure SnO₂ cores and W₁₈O₄₉ branches. Annealing of heterostructures in oxygen atmosphere at 500 °C for 1 h changed the sample color from blue to yellow and the XRD spectra (not shown here) indicated conversion of W₁₈O₄₉ to WO₃ without changing the morphology of the heterostructures. All further characterization and gas sensing measurements were carried out on as grown heterostructures.

TEM images of heterostructures are shown in Fig. 3. Low magnification TEM in Fig. 3a shows that $W_{18}O_{49}$ nanowires have smooth



Fig. 2. XRD spectra of SnO₂:W₁₈O₄₉ nanowire heterostructures.

surface and small reduction in diameter from root to the tip. High resolution TEM confirmed sharp interface between SnO_2 and $W_{18}O_{49}$ (Fig. 3b) and also showed that $W_{18}O_{49}$ nanowires grow along (0 1 0) direction (Fig. 3c).

Effect of growth conditions on the nature of W₁₈O₄₉ nanowires (on SnO₂ nanowires) was investigated and the results are shown in Fig. 4. Density, diameter and length of W₁₈O₄₉ nanowires was found to increase with increase in pressure (Fig. 4a-c and Fig. 1b). This is understandable as increase in pressure leads to higher oxidation rate and thereby increased evaporation rate. Similar results were obtained by increase of filament (tungsten) temperature at fixed pressure. On increasing the temperature of the W foil to 2050 °C (pressure = 2.5×10^{-4} mbar), we observed that SnO₂ nanowires get coated by a thick layer of $W_{18}O_{49}$ resulting in core-shell like structure of SnO₂-W₁₈O₄₉ (Fig. 4d). The results show that the morphology and thus functionality of these hierarchical structures may be tuned by controlling the growth parameters. Further characterization and studies have been carried out on heterostructures formed by deposition of $W_{18}O_{49}$ at a pressure of 2.5×10^{-4} mbar and source temperature of 1965 °C.

SEM images at different stages of growth of W₁₈O₄₉ nanowires (5, 15 and 30 min) were acquired to visualize nucleation and growth morphologies and the results are shown in Fig. 5. It is seen that the size of the nuclei is much larger than diameter of the nanowires. This is in agreement with the growth mechanism of $W_{18}O_{49}$ nanowires proposed by Thangala et al. [21] where the growth occurs by nucleation of WO₂ clusters followed by precipitation of WO_{3-x} crystals having tip of considerably smaller dimensions. Enhanced adsorption of WO₂/WO₃ species on the tip was proposed to result in the growth of nanowires. Partial pressure of oxygen (in 10^{-5} to 10^{-3} mbar range) employed in present study is much less than 0.1-10 mbar used by Thangala et al. [21] and this may help in nucleation of oxygen deficient WO₂ nuclei. We may add that similar vapor-solid mechanism of 1D growth promoted by sub-oxide tip has been used to explain growth of other oxide nanowires like SiO₂ [22]. The mechanism also explains the forma-



Fig. 3. (a) TEM image of a typical SnO₂:W₁₈O₄₉ nanowire heterostructure and HRTEM images showing (b) sharp interface between a typical SnO₂ nanowire and W₁₈O₄₉ nanowire and (c) growth direction of W₁₈O₄₉ nanowires.

tion of core-shell structure (Fig. 4d) at higher tungsten filament temperature (\sim 2050 °C), as high WO₂ super saturation leads to the growth of a continuous layer of WO₂ on SnO₂ nanowires followed by formation of W₁₈O₄₉ shell.

Raman Spectrum of HSNW (Fig. 6) shows three broad bands at 253, 698 and 795 cm^{-1} . The spectrum is very similar to that

reported by Thangala et al. [21] for pure $W_{18}O_{49}$ phase. Bands at 698 and 795 cm⁻¹ are assigned to W–O stretching modes while the band at 253 cm⁻¹ is ascribed to O–W–O bending modes [21,23]. As $W_{18}O_{49}$ structure contains a wide range of W–O–W bond lengths, the Raman peaks are generally very broad [24]. Interestingly, we do not get any peak corresponding to SnO₂, as it is covered with



Fig. 4. SnO₂:W₁₈O₄₉ heterostructures grown at filament temperature of 1965 °C in air at (a) 5×10^{-5} mbar, (b) 9×10^{-5} mbar, and (c) 7×10^{-4} mbar pressure. Also shown (d) are typical heterostructures grown at higher filament temperature of 2050 °C and air at pressure of 2×10^{-4} mbar.



Fig. 5. SEM images obtained at different stages of W₁₈O₄₉ nanowires growth: (a) initial SnO₂ nanowires and growth after (b) 5, (b) 15, and (d) 30 min. A schematic diagram corresponding to each stage of growth is also shown below SEM images.

 $W_{18}O_{49}$ nanowires [25]. Raman analysis further indicates absence of interaction of $W_{18}O_{49}$ with SnO₂.

XPS spectra of heterostructures are shown in Fig. 7. Sn $3d_{5/2}$ and $3d_{3/2}$ peaks show essentially symmetric lines with binding energies at 486.4 and 494.7 eV that are assigned to Sn⁴⁺ in SnO₂. This indicates that the nanowires consist of pure SnO₂ phase. On the other hand, W 4f spectrum shows a broad peak due to merging of $4f_{7/2}$ and $4f_{5/2}$ lines. This has been deconvulated into six peaks indicat-



Fig. 6. Raman Spectrum of as deposited $SnO_2:W_{18}O_{49}$ nanowire heterostructures plotted as intensity of scattered light as function of Raman frequency shift.



Fig. 7. XPS spectra of as deposited $SnO_2:W_{18}O_{49}$ nanowire heterostructures plotted as intensity of electrons as function of binding energy (equal to difference of incident photon energy and kinetic energy of emitted electrons; data plotted after correction for spectrometer work function).

ing tungsten in multiple chemical states of W⁺⁶, W⁵⁺ and W⁴⁺ as reported in some earlier studies [26,27]. This further confirms that tungsten oxide in W₁₈O₄₉ phase. The O 1 s spectrum has been deconvoluted into two peaks at 530.6 and 532.0 eV that are attributed to inorganic oxides (SnO₂ and WO₃) and adsorbed oxygen, respectively. There could also be small amount of adsorbed carbonate or hydroxide groups. XPS spectra of the heterostructures also indicate the presence of pure SnO₂ and W₁₈O₄₉ phases and absence of interaction between them.

Isolated HSNW sensors (type-A) were investigated for response to various gases and quite interesting results were obtained. The results were compared with those on mat type heterostructure sensors (type-B) and pure SnO_2 single wire (type-C) and mat type (type-D) sensors. For comparison response of $W_{18}O_{49}$ thin films was also measured for different gases. The results may be summarized as follows:

- 1. Type A sensors (typical SEM image shown in Fig. 8a) showed very good response and high selectivity for the detection of chlorine at room temperature. Typical response of a sensor to chlorine is shown in Fig. 8b and c. (Here, response is plotted as normalized current $N_I = I/I_a$; where, *I* is the measured current as function of time and I_a is the current in air; all measurements at a fixed voltage) The sensor shows a response ($S = I_g/I_a$) of ~1.1 for 0.25 ppm and 11.0 for 6 ppm of Cl₂ gas. The response and recovery times for 6 ppm Cl₂ are found to be 4.6 min and 17 min, respectively. The sensors showed a detection limit (concentration where noise is nearly equal to change in resistance) of ~ 0.1 ppm of Cl₂. The sensors showed negligible response to $H_2S(S \sim 1.15 \text{ for } 6 \text{ ppm of})$ gas) and no response to CO, NO_x and NH₃ gases. Apart from high sensitivity and selectivity for chlorine, it is seen that the response is anomalous in that the resistance reduces on exposure to oxidizing gas (chlorine) as is normally observed for reducing gases [18].
- Single wire SnO₂ sensors (Type-C) showed highly increased response for detection of H₂S but similar response for detection of chlorine (Fig. 9). Both gases showed decrease in resistance similar to single HSNW sensor indicating anomalous response to chlorine in this case as well.
- Both of the mat type sensors (types B and D) showed increase in resistance (Fig. 10b and d) for chlorine and decrease for H₂S (Fig. 10a and c) as is normally expected on exposure of n-type semiconductor sensors to oxidizing and reducing gases, respectively [28].
- 4. Response of $W_{18}O_{49}$ thin films on exposure to 1 ppm of Cl_2 and 20 ppm of H_2S (data not shown here) was found to be 0.8 and 1.01, respectively. No measurable response was found on exposure to 1 ppm of H_2S gas.





Fig. 8. (a) Single heterostructure nanowire aligned between two gold electrodes for gas sensitivity measurements. Inset shows expanded view of heterostructure. (b) and (c) Normalized current ($N_I = I/I_a$) as a function of time for an isolated HSNW sensor on exposure to different concentrations of Cl₂ gas at room temperature.

First, we try to understand anomalous response to chlorine for single wire sensors of pure SnO_2 and HSNW. We note that response of polycrystalline semiconductor sensors generally has two distinct contributions, i.e. from intragrain regions and grain boundaries. Single wire sensors have only intragrain contribution while mat type sensors have both intragrain and grain boundary contributions. Comparison of mat type and single wire responses indicates that grain boundary regions have normal response to chlorine while intragrain contribution is anomalous. Four different interactions of



Fig. 9. Normalized current $(N_I = I/I_a)$ as a function of time for pure SnO₂ single nanowire sensor on exposure to (a) 4 ppm Cl₂ and (b) 4 ppm H₂S gas at room temperature.

chlorine with semiconductor oxides have been reported [29]

$$\frac{1}{2}Cl_2 + O_{(ad)}^{2-} \to Cl_{(ad)}^- + \frac{1}{2}O_2 + e^-$$
(1)

$$\frac{1}{2}Cl_2 + O_0^{2-} \to Cl_0^- + \frac{1}{2}O_2 + e^-$$
(2)

$$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-_{(ad)} \tag{3}$$

$$\frac{1}{2}Cl_2 + e^- + V_0 \to Cl_0^- \tag{4}$$

where subscripts (ad) and O indicate species adsorbed on surface of semiconductor oxide particles and species occupying oxygen lattice site, respectively and V₀ indicates vacancy at oxygen site. Reactions (1) and (2), where chlorine replaces lattice or surface adsorbed oxygen yield anomalous response with resistance decreasing on exposure to chlorine. On the other hand reactions (3) and (4), where chlorine is adsorbed at surface or at oxygen vacancy site yield normal response with resistance increasing on exposure to chlorine. Results indicate that in the case of single wires that are crystalline, reaction predominantly occurs with lattice oxygen and oxygen adsorbed on surface leading to anomalous response. Additional sites for chlorine adsorption are not available due to low defect density. On the other hand, in the case of mat type sensors, there are large numbers of defect sites between the grains on which additional chlorine may be adsorbed leading to normal response to chlorine with increase in resistance.

Good sensitivity to chlorine and reduced sensitivity to H_2S for type A sensors may be understood with respect to ideal $SnO_2:W_{18}O_{49}$ hetero-junction band diagram shown in Fig. 11 [30]. Typical values of electron affinity and work function of WO₃ and SnO_2 has been taken from literature [31]. It is seen that electron density is enhanced in SnO_2 near the junction while it is reduced in $W_{18}O_{49}$. The width of region with enhanced electron density (region marked as A) near junction in SnO_2 is expected to cover nearly full nanowire cross-section as the diameter of nanowires is much smaller than typical depletion layer width. Typical depletion layer width on SnO_2 side was calculated using the theoretical expression [32]

$$L_{\rm depl} = \frac{\varepsilon_0 \varepsilon_r}{e n_{\rm s}} (V_{\rm bi} - V)$$

where ε_0 is the vacuum permittivity, ε_r is the dielectric constant of the ambient semiconductor, e is the elementary charge, n_s is the two-dimensional carrier density, V is the applied potential and $V_{\rm bi}$ is the built-in potential. The carrier density has been taken as 10^{17} cm⁻³ and ε_r for SnO₂ as 15 [33]. The width on SnO₂ side with zero applied voltage was calculated to be 0.9 µm as compared to typical diameter of nanowires of 150 nm.

In single wire sensors, conduction takes place through SnO₂ wire as W₁₈O₄₉ wires forming branches on SnO₂ stem are not connected to each other. From band diagram, it is observed that electrons in $W_{18}O_{49}$ are at higher energy than those in SnO₂. Response to chlorine occurs by reactions (1) and (2) taking place in $W_{18}O_{49}$ and SnO_2 . As the electrons generated in $W_{18}O_{49}$ are transferred to SnO₂, a large change in resistance of SnO₂ nanowire occurs, resulting in good sensitivity of Type-A sensors to chlorine. To understand highly reduced sensitivity to H₂S, we note that (a) air resistance of SnO_2 nanowires (with $W_{18}O_{49}$ hetero-junctions) is reduced in comparison to pure SnO₂ nanowires due to electrons injected from $W_{18}O_{49}$ and (b) interaction of H_2S with $W_{18}O_{49}$ is low as $W_{18}O_{49}$ nanowires are already oxygen deficient and W₁₈O₄₉ is not as good a H_2S sensor as SnO_2 [8a]. Poor sensitivity of $W_{18}O_{49}$ to H_2S is also indicated by our measurements on $W_{18}O_{49}$ thin films (data given above). If number of excess carriers generated on interaction with H_2S is assumed to be same (as for pure SnO_2 nanowires)



Fig. 10. Normalized current ($N_l = l/l_a$) as a function of time for mat type sensor films at room temperature on exposure to 8 ppm of different gases. Pure SnO₂ film exposed to (a) H₂S and (b) Cl₂. Heterostructure nanowire film exposed to (c) H₂S and (d) Cl₂.



Fig. 11. Energy band diagram for (a) isolated $W_{18}O_{49}$ and SnO_2 materials and (b) the corresponding heterojunction band structure for an ideal interface (i.e. charge exchange is Fermi level mediated). Ideal charge exchange results in the formation of a macroscopic negative dipole as indicated by ξ . Region A has enhanced electron density in SnO_2 and region B has reduced electron density in $W_{18}O_{49}$. Region A with enhanced electron density may cover full nanowires as typical depletion layer width exceeds nanowire thickness.

the relative change in resistance is low due to lower base resistance. Good response to chlorine and simultaneous lower response to H_2S explains improved selectivity of single wire hetero-junction sensors.

4. Conclusions

Nanowire hierarchical hetero-structures of SnO₂:W₁₈O₄₉ have been prepared by thermal evaporation technique. The density of $W_{18}O_{49}$ nanowires was found to depend on partial pressure of oxygen and source temperature. Single wires of heterostructures have been aligned between two electrodes to make gas sensors that show high sensitivity and selective response to chlorine gas at room temperature. Improvement in selectivity is attributed to transfer of electrons from $W_{18}O_{49}$ to SnO_2 on formation of heterojunctions. The study shows potential of semiconductor oxide hetero-junctions for application to sensors and other electronic devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2010.04.016.

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