Chapter 2

SnO$_2$-WO$_x$ hierarchical nanoheterostructures—synthesis, characterization and gas sensing studies

2.1 Introduction

2.2 Experimental

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The chapter deals with the synthesis of hierarchical nanoheterostructures of SnO₂-WOₓ by a simple two step thermal evaporation technique. The synthesis of SnO₂ nanowire was optimized earlier in our group at TPD, BARC by furnace growth route. Here, the growth of WOₓ nanowire heterostructures on the synthesized SnO₂ nanowires is presented. The synthesis is carried out by thermal evaporation of tungsten (W) foil under low vacuum (10⁻⁴ mbar) conditions. The growth of WOₓ nanowires on SnO₂ nanowires is optimized as a function of a) deposition time b) filament (W foil) current and c) the gas pressure inside the chamber.

The size of nanowire heterostructures is investigated by using SEM. The diameter of WOₓ nanowires on SnO₂ is found to be around 50 nm (±10 nm) and the length was about 1-2 µm (±500 nm). The samples are characterized by using Uv-Vis absorption, XPS, XRD and HRTEM. The bandgap of the material is observed to be 3.6 and 2.5 eV respectively. The junction between SnO₂ core and WOₓ branches is studied by using HRTEM and it is confirmed that there is a sharp interface between SnO₂ and WOₓ and the absence of mixed or alloy phases in the sample. The samples are crystalline in nature as observed in XRD.

The growth mechanism of SnO₂-WOₓ nanoheterostructures is elaborated in the discussion section. A preliminary study on the utility of these nanoheterostructures is investigated by studying the gas response to oxidizing and reducing gases. (Cl₂ and H₂S gas). The SnO₂-WOₓ nanowire bundles in the form of films (mat films) and single wires are tested for gas sensing study. Comparative gas sensing study with pure SnO₂ mat films suggests that the addition of WOₓ provides selectivity towards detection of Cl₂ gas at room temperature. The improved selectivity is attributed to the electron transfer from WOₓ to SnO₂ in the presence of Cl₂ gas.
2.1 Introduction

There is a growing concern by the world community for the global protection of the environment, in particular the air we breathe.

People, especially in urban areas, are exposed to a high quantity of harmful gases at work, in traffic and at home. In order to address the environmental pollution due to hazardous gases, a wide range of gas sensors based on a diversity of materials, technologies and design, has been developed [1, 2]. However, ever heightening environmental concerns of our society are resulting into more stringent regulations which provide a sustained impetus to the current interest and activity in the research and development of gas sensors. These are made from a variety of materials like catalytic combustion gas sensors, solid electrolyte gas sensors and semiconductor oxide based gas sensors. Many applications, such as an automobile exhaust gas control or air conditioning, as well as household food processing or private diagnosis, demand extremely cheap, long-term reliable and analytically powerful gas-sensor devices [3].

Apart from the economy they offer, sensors made of semiconductors have been investigated most extensively, because of their chemical stability and large variation in electrical resistance with the changing atmospheric gases and long service life. The metal oxide semiconductors in particular, are one of the most versatile materials due to their diverse properties and functionalities such as wide bandgap, chemical stability, etc. [4].

The history dates back to 1938 when Wagner and Hauffe discovered that atoms and molecules interact with semiconductor surfaces and influence their conductivity and surface potential. The effect of ambient upon the electrical conductance of semiconductors was described by Brattain and Bardeen (1953), Heiland (1954) and Morrison (1955). Subsequently, Seiyama et. al. (1962) and Taguchi (1970) applied this
discovery to gas detection by producing the first chemo-resistive semiconductor gas sensor [5].

The most suitable semiconductor materials for this type of sensors are transition metal oxides. Typical metal oxides include SnO₂ [6], ZnO [7], TiO₂ [8], etc. Some oxides are used as modifiers like Fe₂O₃ [9], WO₃ [10], CuO [11], MoO₃ [12] and In₂O₃ [13]. Unlike other semiconductors which, under long-term or cycled heating in air, undergo irreversible chemical transformations by forming stable oxide layers, metal oxides bind oxygen on their surface which can be removed under certain conditions in a reversible way.

Metal oxide sensors are commercially available from many years. The leading manufacturer is Figaro Engineering in Japan, the type of metal-oxide sensor sold by Figaro is known as the "Taguchi sensor", named after the developer of the SnO₂ sensor. Metal oxide sensors operate by decreasing the resistance of a layer of ceramic, e. g. SnO₂ sensor if a reducing gas is present in the ambient. Some promoters like Pt, Pd and Ag are used [14]. They are sensitive to the environmental changes and show a change in their resistance through mainly the surface related phenomena. A reduction in the size of sensing element like metal oxide particles improves its sensitivity, which may also affect the operating temperature [15].

The study of SnO₂ as gas sensing material is due to its suitable physicochemical properties as, for example, it has a high reactivity to reducing gases at relatively low operating temperatures. Moreover, SnO₂ has a lower cost as compared to available materials for similar applications. Nowadays, the research on gas sensing materials is focused to increase the sensitivity, selectivity and stability [15].

The principle of operation of SnO₂ semiconductor gas sensor lies in detecting the conductivity changes experienced by the n-type material when surface chemisorbed oxygen reacts with gases, such as H₂ or CO. [16, 17].
In n-type semiconductors such as SnO₂, a two-step process has been suggested for the electrical response to reactive gases. First, oxygen from the ambient adsorbs on the exposed surface of the grains, and extracting electrons from the material, ionizes to O⁻ or O²⁻. The species, O⁻, is believed to be dominant, because (i) the doubly charged state of oxygen may lead to instability, unless the site has a large Madelung constant, and (ii) due to high reactivity of O⁻; O²⁻ is not expected to react significantly with the ambient gas, and at moderate temperatures may transform to O⁻. The extraction of electrons leads to the formation of a depletion region at the intergranular contact as depicted below. For electrical conduction, electrons must pass from grain to grain and cross the barrier at the intergranular contacts. Thus, the sensor surface is highly resistive. A reducing gas such as CO then reacts with the adsorbed oxygen producing CO₂, and injects electrons back into the conduction band, thereby decreasing the barrier height and resulting in the increase in conductivity. [17a].

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2.1.1 Motivation for the present work

Bulk properties such as piezoelectricity, chemical sensing and photodetection of metal oxide materials are further enhanced in their Quasi one dimensional (Q1D) form due to geometry and carrier confinement. In the nano-scale, the surface to volume ratio of the metal oxides is increased. The increased surface area provides more number of active sites for the reaction of test gases. Therefore nanostructures of metal oxides are promising candidates for gas sensing.

In this respect, various oxide nanostructures have been explored, including nanoparticles (0D) [8, 13], thin films [9, 21, 22], nanowires (1D) [16], nanotubes (1D) [18], nanobelts (quasi 1D) [19] and nanocubes (3D) [20]. In the above references, the synthesis and their gas sensing study of different materials has been discussed extensively. A brief overview is presented here.

The synthesis of TiO₂ nanoparticles and nanotubes by techniques such as sol-gel method, anodic alumina deposition (AAM), hydrothermal method, solvothermal method, direct oxidation route have been carried out [8]. The structural, thermal, electronic and optical properties of TiO₂ nanomaterials were reviewed in the report, besides due to well-known quantum-confinement effect these nanomaterials demonstrate size-dependent as well as shape- and structure-dependent optical, electronic, thermal and structural properties. Thin films of SnO₂ and WOₓ (separately) were tested for gas sensing and their sensing devices were presented [14]. The synthesis of SnO₂-CuO composite films was presented [21]. It was presented in the report that SnO₂ and CuO are mutually non reactive. The sensitivity of SnO₂ to H₂S gas has been improved due to addition of CuO [21]. The formation of CuO nanowires by thermal oxidation in the presence of oxygen atmosphere has been carried out and the morphology and the microstructures of the samples were studied by using various
characterization techniques [17]. The doping of CuO into SnO₂ nanowires has been carried out and it has improved the sensitivity to H₂S gas [22].

Further, nanowire sensors have demonstrated significantly higher sensitivity at lower temperature [21, 22] an advantage over thin film gas sensors, which are usually operated at elevated temperature. For example thin films of SnO₂-CuO-SnO₂ were prepared in the ratio of 10:1:10. The sensitivity of the films was $25 \times 10^3$ [sensitivity defined as the ratio of resistance of the film in the presence of air to that in the presence of 50ppm H₂S Gas] (maximum normalized output) at 200 °C [measured in the temperature range of 140-260 °C] for 50ppm H₂S gas [21]. In case of nanowires films the Cu doping of upto 16 % was observed. The sensitivity of the order of $10^6$ times (sensitivity = Ra/Rg) was observed for 50 ppm H₂S gas at 150°C [22]. Therefore it can be said that Q1D metal oxide semiconductor based gas sensors surpass other chemical sensors for better sensitivity compared to their thin films due to large surface to volume ratio. This reduces the complexity of sensor design and power consumption. These include carbon nanotubes, SnO₂ nanowires or nanobelts, In₂O₃ nanowires, WO₃ nanorods etc [9-23]. However, metal oxide nanowire sensors also suffer from the drawback of low selectivity for detection of different gases. The response is measured generally in the form of change in conduction in the presence of oxidizing or reducing gas.

Doping of metal oxide, i.e. addition of another metal oxide in a very small amount to metal oxide nanowires has shown to improve the gas sensing properties [22]. Mixing of a metal oxide into another metal oxide nanostructure in the form of additive has been demonstrated to possess different properties [31]. For example V₂O₅ heterostructures formed on SnO₂ nanowires resulted in the photoconduction of the material being different from that of pure SnO₂ nanowires [31]. This is attributed to the local modification of the electronic properties of the host material.

Q1D structures can be used as templates for the growth of other nanostructures leading to the formation of novel nano heterostructured
materials. Formation of heterostructures results in the possibility of enhancing the functionality of 1D structures.

A 'hierarchical structure' means the higher dimension of a micro- or nanostructure composed of many, low dimensional, nano-building blocks. For example, 3D hierarchical heterostructures means that 1D nanowires/nanorods are assembled into a 3D urchin-like spherical shape [24].

Growths of various types of nanowire heterostructures have been reported and a brief review of which is presented here. Synthesis of core/shell nanowire structures of Si core and CdS shell using pulsed laser deposition for light emitting diodes was reported. A successful LED fabrication was presented despite the fact that optimization of synthesis was not done. The diameter of Si 100 nm and shell thickness was about 50 nm [25]. Coaxial nanocables were reported by Li et. al. wherein SiC-SiO₂-C coaxial cables were synthesized [26]. In another report on coaxial nanowire, synthesis of heterojunctions of InAs and InP by using chemical beam epitaxy was presented. The rapid alternation of the composition was controlled by the supply precursor atoms into the eutectic melt, supplied as molecular beams into ultrahigh vacuum chamber. The diameter of the synthesized nanowires was about 50 nm. This was the first measurement of a designed heterostructures potential within 1D system [27].

Hierarchical heterostructures of Si core and SiO₂ nanowires have been reported by vapor liquid solid growth mechanism for optical study such as photoluminescence [28, 29]. SnO/SnS was used that acts as a catalyst in the above synthesis. The diameter of the core nanowires was about 200 nm. The cathode luminescence of the samples was tested further [26, 27]. The diameter of the nanowires was about 50 nm with a Si drop at its tip. Hierarchical heterostructures consisting of nanowires grown on larger nanowire stem were of interest due to their potential in the realization of three dimensional nanodevices. The cores and branches of these nanostructures were of different materials with different band gap and
work function. Synthesis of these hierarchical structures by thermal evaporation using mixture of ZnO with other semiconductors has been reported. The heterostructures formation of ZnO on other (Carbon structures, GaN, GaP, SiC, SiC-C nanostructures), one-dimensional structures was carried out by using thermal chemical vapor deposition technique [30]. Some heterostructures of SnO2 in combination with other semiconductors have also been recently reported [31-34]. V2O5 branched nanowires have been grown on SnO2 nanowires [31]. In this report the molecule assisted gold catalyzed chemical vapor deposition was implemented to obtain aligned SnO2 nanowires that act as a template for the growth of V2O5 nanowires. The V2O5 nanowires were grown either parallel or vertical to the SnO2 nanowires. Photoluminescence was studied further in the report. SnO2 nanorods have been prepared on α-Fe2O3 nanotubes by using a facile solution method. The lattice mismatch during the growth played a vital role in deciding the growth direction. The dimensions of the SnO2 nanowires structures were of the order of about 200 nm length and diameter of about 50 nm [32]. One-dimensional (1D) SnO2 nanostructures on pre-synthesized ZnO tetrapods were grown by thermal evaporation [33, 34]. In most of these reports the synthesis of the heterostructures and their optical characterizations were presented. Many of the reported synthesis were carried out using metal catalysts that introduce impurities into the system. Further, not much has been reported on applications and devices based on heterostructures.

2.1.2 Present Work

Motivated from the results on heterostructures, the work on synthesis and characterization of SnO2-WOx hierarchical heterostructures without
use of catalyst and their application as selective chlorine sensor at room
temperature is presented in this chapter.

Nanorods of transition metal oxide such as WO$_3$, are promising
candidates for a vast range of applications including gas sensors [gases
such as ammonia vapors, hydrogen sulfide, and hydrocarbons],
photocatalysts, electrochromic devices, field emission devices and solar
ergy devices [35, 36, 37]. They have demonstrated novel sensing
properties such as high sensitivity, fast response time and low operation
temperature. Tungsten oxide nanowires have been synthesized by heating
tungsten in various forms (plates, wires and powders) [35]. The synthesis
of tungsten oxide and metallic tungsten nanowires using oxygen flow over
hot filaments onto the substrates maintained at different temperatures is
reported. The studies have shown that the tungsten oxide nanowires were
formed when condensation of vapor phase metal oxide species occurred on
the substrates. The growth mechanism is thermal oxidation [36].

In the present work, heterostructures of WO$_X$ are synthesized on pre
synthesized SnO$_2$ nanowires. The combination of SnO$_2$ and WO$_X$
nanostructures was reported in other groups, has improved the selectivity
for NO$_2$ gas and the sensor was operable at lower (100-300 °C) temperature
[10]. WO$_3$-SnO$_2$ nanocomposites of various compositions have been
successfully synthesized by a controlled two-step sol-precipitation method
using tin chloride and ammonium metatungstate hydrate as precursors.
The sensing mechanism of the NO$_2$ sensor is attributed to chemical and
electronic synergistic effects of components.

The combination of the two metal oxides in the nanostructure form can
be achieved in two ways by 1) loading the tungsten metal powder and tin
metal powder at the same time as a source. 2) Hierarchical
nanoheterostructure formation of one metal oxide over the other. (Using
one synthesized metal oxide as a template for the growth of another metal
oxide onto it). In both the methods, n-n junctions can be achieved. In case
of heteronanostructure formation of one metal oxide nanowires over the

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other provides more number of active sites for the interaction with the
gaseous species (effective area for gas adsorption is increased) therefore is
implemented in the present study. This is the first report, to the best of our
knowledge, on hierarchical heterostructures of SnO$_2$-WO$_x$.

The SnO$_2$-WO$_x$ hierarchical heterostructures were characterized by
using SEM, XPS, XRD and TEM. The gas sensing study is carried out
further for single wires and for mat films of the heterostructures. The
single wire isolation is implemented to the best of our knowledge for the
first time in the country; using optical microscopy method described in
detail in experimental section. Our results on gas sensing of SnO$_2$: WO$_x$
heterostructures show that tailored nano-heterostructures with possibility
of carrier transfer from one material (WO$_x$) to another (SnO$_2$) may be
employed for the development of various selective gas sensors.

2.2 Experimental

The SnO$_2$-WO$_x$ hierarchical nanoheterostructures are synthesized by using
a simple two step thermal evaporation technique. The synthesis of SnO$_2$
nanowire is discussed first and then the synthesis of SnO$_2$-WO$_x$ nanowire
heterostructures is presented.

2.2.1 Synthesis of SnO$_2$ nanowires

SnO$_2$ nanowires are grown by furnace growth route. The schematic of the
experiment is represented in Figure 2.1. A 99.9% pure tin metal powder
approximately 2 gm by weight was placed in an alumina boat. The boat
was inserted inside the furnace with an inbuilt thermocouple. A high
purity Ar gas was allowed to flow through the furnace at the rate of 1000
sccm. (The Ar gas consists of 1% or less traces of oxygen for the oxidation of metal tin powder). The gas flow inside the tube was controlled by using a standard gas flow controller. The target temperature was optimized to 900 °C and growth time was one hour. The rate of heating and cooling of the furnace is 300 °C/hr. The schematic of the furnace is presented in Figure 2.1. It is an evaporation condensation growth mechanism as mentioned on page 50 in result section. SnO₂ nanowires are formed on the surface of the alumina boat on the top of the source material as shown in Figure 2.2a).

![Furnace systems](image)

**Figure 2.1 Furnace systems**

### 2.2.2 Synthesis of SnO₂-WOₓ nanowire heterostructures

The SnO₂ nanowires synthesized by the above mentioned method were placed at the position of substrates and used as template for the growth of WOₓ nanowires. The hierarchical nanoheterostructures of SnO₂-WOₓ are
synthesized by using thermal evaporation technique as shown in Figure 2.2. The system consists of a rotary pump backed by a diffusion pump and vacuum level achieved inside the chamber was about $10^{-5}$ mbar. During growth, the pressure was maintained to $10^{-4}$ mbar by inletting atmospheric air inside the chamber using a needle valve. A tungsten foil of 4 cm length and 1 cm width was used as a source. It was heated to about 1800 °C. The SnO$_2$ nanowires were not deliberately heated but during deposition their temperature increased to 700 °C. The distance between the filament and the template was initially varied between 1.5 to 2.5 cm. Not much of change in the morphology of heterostructures was obtained. Therefore the distance between the filament and the substrate was maintained to 2 cm for all further experimentation.

![Thermal evaporation system](image)

**Figure 2.2 Thermal evaporation system**

Controlled growth of ZnO nanostructures on SnO$_2$ nanobelts was carried out by Sun et. al.[34]. It was believed in the report that the growth temperature and gas phase supersaturation determines the growth rate of surface planes and the final morphology of the crystals. Higher temperatures favor the growth of ZnO nanobelts, while ZnO nanowires were formed at relatively low temperatures. The optical studies were
carried out further. This study motivated us to increase the temperature and growth time in the present problem, to study its effect on the WO$_x$ nanowire growth on SnO$_2$ nanowires.

The optimized parameters for the growth are as follows

2.2.3 **Effect of filament current/filament temperature**

In order to see the effect of filament current, the other two parameters i.e. growth time and vacuum conditions have to be fixed. The current allowed through the tungsten filament was increased systematically between 50 A to 85 A in order to study its effect on growth of WO$_x$ nanowires.

2.2.4 **Effect of variation in vacuum conditions**

Under optimized filament current, the gas pressure inside the chamber was increased by systematically varying from $5.5 \times 10^{-5}$, $9 \times 10^{-5}$ and $7 \times 10^{-4}$ mbar in the presence of air and oxygen by using the needle valve. During the pressure variation the filament current and the growth time were kept constant at 80 A and 30 minutes respectively.

2.2.5 **Effect of growth time**

To get an idea about the nucleation, crystal formation and the nanowires structure formation the growth time for the deposition of WO$_x$ was varied as 5, 15 and 30 minutes. The filament current, growth time and air pressure inside the chamber was optimized previously to 80 A, 30 minutes and $2 \times 10^{-4}$ mbar, respectively.

2.2.6 **Fabrication of gas sensors**
The nanoheterostructures of SnO$_2$-WO$_x$ formed were tested for their gas sensing response in two forms:

1. Mat
2. Single wire

### 2.2.6.1 Preparation of mat film

The mat films were prepared by dispersing the SnO$_2$-WO$_x$ nanoheterostructures in methanol to form slurry. The slurry was pressed manually on an alumina piece to form a film. Contacts were made on the film by depositing gold by using thermal evaporation technique. The vacuum of about 10$^{-5}$ mbar was maintained and the thickness of gold was about 500 Å. The thickness of gold pads was calculated by measuring amount of material kept in the boat and the distance between the source and the substrate. The contacts leads were made by using silver wires. The wires were fixed on the films by using room temperature operable Ag paste as mechanical as well as electrical support to the contacts.

### 2.2.6.2 Preparation of Single wire sensor

The single wire sensors were obtained by using optical microscope as described below. Single wire isolation has been carried out for the first time to the best of our knowledge in India, using this method. The SnO$_2$-WO$_x$ nanoheterostructures were dispersed in methanol and a dilute solution was prepared. The sample was drop casted on a glass slide and observed under a microscope. A single nanowire of hierarchical heterostructures was identified under the microscope (Metzer optic 780-2335); while observing, a mask of 12 µm was placed onto it. Gold was deposited on the films by thermal evaporation as described above. The mask (12 µm) was
slowly removed from the film by using forceps. Silver wire contacts to the film were made by using room temperature curable silver paste. The change in electrical resistance with respect to the test gas is measured for the gas sensing study. In the isolated single wire, diameter of SnO₂ is about 500 nm and that of WOₓ is about 50 nm.

2.2.7 Testing of gas sensors

The 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 the films was measured (under changing gaseous atmospheres) for a constant voltage applied across the gold pads using Kiethley picoammeter in the presence and absence of gas with respect to time.

2.3 Results and discussion

The results on SnO₂ pure nanowires are discussed first. The hierarchical heterostructures are described in the next section.

2.3.1 SnO₂ nanowires

It is observed that white wool like growth of SnO₂ nanowires occurs on the top of the entire boat (Figure 2.2 a)). The SEM of SnO₂ nanowires on the alumina boat surface is shown in Figure 2.2b). The diameter of SnO₂ nanowires near the boat surface is large of the order 2-5 μm and it makes a support like structure for the growth of SnO₂ nanowire. The diameter of SnO₂ nanowires at the tip is about 50-170 nm and length is varying to few microns as shown in Figure 2.2c).
The growth of SnO$_2$ nanowires is via a simple evaporation condensation reaction. In order to observe the growth on the boat walls a small alumina substrate was mounted vertically on the alumina boat wall by using alumina paint. SnO$_2$ growth was taken onto the same and placed the sample vertically on the substrate holder in SEM. It was observed that, the prolonged condensation at the boat walls leads to a thick nanowire formation as shown in Figure 2.2b). The XRD of the pure SnO$_2$ nanowire samples is presented in Figure 2.2d). The sharp peaks in the XRD shows that the samples are polycrystalline in nature and having rutile (tetragonal)
phase with lattice constants \( a = 4.750 \) and \( c = 3.196 \) Å (PCPDF Card Number 770451).

This confirms that the sample is pure SnO\(_2\) and it can be used as a template for the further growth of WO\(_x\) wires.

### 2.3.2 SnO\(_2\)-WO\(_x\) nanowires heterostructures

The SnO\(_2\) nanowires were used as substrate/template for the growth of WO\(_x\) nanowire heterostructures. The vacuum achieved inside the jar was \( 10^{-5} \) mbar. The surface of the tungsten filament was slowly oxidized by inletting atmospheric air/oxygen by using needle valve to \( 10^{-4} \) mbar. The growth time was fixed to 30 minutes.

The deposition of tungsten oxide on SnO\(_2\), changes the colour of the sample from white wool like to deep blue.

#### SEM studies

**2.3.2.1 Effect of filament current**

In order to study the filament current effect (deposition rate) on the growth of WO\(_x\) nanowires; three parameters i.e. the distance between the source and template, growth time and vacuum conditions were fixed initially. The filament current was maintained to 50 A for 30 minutes; absence of WO\(_x\) nanowires growth was observed on the surface of SnO\(_2\) nanowires (Figure 2.3a)). For a current of 60 A, the growth of WO\(_x\) nanowires with very small dimensions occurs on the surface of SnO\(_2\) nanowires (Figure 2.3 b)). Further increase in the filament current i.e. at 75 A, WO\(_x\) nanowires on the surface of the SnO\(_2\) nanowires with diameters of the order of 50 nm and length of approximately 200 nm were obtained (Figure 2.3c)).

In order to improve the length of WO\(_x\) nanoheterostructures the filament current is increased to 80 A. The diameter of WO\(_x\) nanowires is remaining
the same at around 50 nm while the length is increased to 1.5-2 μm as shown in Figure 2.3. The filament current is increased up to 85 A and it was observed that core shell like structures with diameters in the micron range are obtained (Figure 2.3e)). From all the SEM pictures it can be concluded that, with the increasing filament current the deposition rate of WOx is increased and that decides the structure formation of hierarchical nanoheterostructures. The core-shell structures formed are thick, with diameters in the micron range.

2.3.2.2 Effect of gas pressure

The tungsten oxide is volatile and evaporates at low melting point (1473 °C for WO3, 1700 °C for WO2) than tungsten (3422 °C); therefore low vacuum conditions are needed. The work on WOx film depositions is carried out by oxidizing the surface of the tungsten foil [37]. The oxidized surface of the tungsten foil sublimes after increasing the temperature. The vacuum should be sufficient to oxidize the tungsten filament, at the same time to avoid the impurity and other unwanted air molecules inside the chamber. Therefore the pressure inside the jar is tried to optimize in the presence of air and oxygen. The gas pressure inside the chamber is optimized by systematically varying from 5.5×10⁻⁵, 9×10⁻⁵ and 7×10⁻⁴ mbar in the presence of air and oxygen. The filament current and growth time was kept fixed at 80 A and 30 minute respectively. The change in gas pressure affects the formation of WOx heterostructures (Figure 2.4 and 2.5).
Figure 2.3 a) 50 b) 60 c) 75 d) 80 e) 85 A current for 30 minutes

In presence of air atmosphere at the pressure of $10^{-5}$ mbar, there is a small growth on the surface of SnO$_2$ nanowires. At $9 \times 10^{-5}$ mbar of air pressure the oxygen content in the chamber is increased therefore long WO$_x$ nanowires were grown on the surface of SnO$_2$. The length is about 2 $\mu$m and the diameter is about 50 nm. At the air pressure of $7 \times 10^{-4}$ mbar, thick thorn like structures of WO$_x$ are formed on SnO$_2$ nanowire surface (Figure 2.4 c)). The diameter of WO$_x$ structure is about 100 nm and the length is
about 1 \mu m. With the increase in gas pressure, the percentage of oxygen in the chamber goes on increasing, that induces oxidation of tungsten foil. The experiments were carried out under the same pressure conditions in oxygen atmosphere. In presence of oxygen pressure of $5 \times 10^{-5}$ mbar, the growth of WO$_X$ occurs on the surface of SnO$_2$ with length of about 1 \mu m with diameter of about 30 nm. It can be seen from the SEM that, the dimensions of WO$_X$ nanowire structures increase with the increase in partial pressure of oxygen. It is possible that, at higher oxygen partial pressure the oxide layer formation on tungsten foil is thicker. The evaporation rate may be higher and therefore fast deposition of WO$_X$ occurs on the surface of SnO$_2$ nanowires. Therefore core shell like structures would have obtained at $5 \times 10^{-4}$ mbar oxygen pressure. From these reasoning it can be confirmed that, the increased pressure of oxygen induces increase in diameter, number of WO$_X$ nanowire i.e. density and length of the WO$_X$ nanoheterostructures.

### 2.3.2.3 Effect of growth time

The synthesis of ZnO hierarchical nanostructures grown on various one dimensional structures (C, GaN, GaP, SiC, SiC-C) was reported [30]. The deposition was carried out by thermal chemical vapor deposition technique and the length of ZnO nanorods increased with the increasing deposition time. Motivated from this, in order to have an understanding of the growth mechanism, the growth time of WO$_X$ was increased systematically between 5, 15 and 30 minutes (Figure 2.6). The steps by step increase in the growth time gives an idea about the nucleation, crystallite formation and the nanowires structure formation.
Figure 2.4 SEM of SnO$_2$-WO$_x$ in presence of a) 5.5x10$^{-5}$ b) 9x10$^{-5}$ c) 7x10$^{-4}$ mbar air

Figure 2.5 SEM of SnO$_2$-WO$_x$ in presence of a) 5x10$^{-5}$ b) 9x10$^{-5}$ C) 5x10$^{-4}$ mbar oxygen
With the increase in growth time the length of WO$_x$ nanowires continues to increase. It can be concluded that the filament current, gas pressure and deposition time plays a vital role in deciding the size and shape of WO$_x$ nanoheterostructures on SnO$_2$ nanowires.

Figure 2.6 a) 5 b) 15 c) 30 minutes deposition.

The change in parameters such as vacuum conditions, growth time and filament current could have induced structural, chemical changes in the material of hierarchical nanoheterostructures. Owing to that the surface area and the chemical composition of the nanoheterostructures might have changed. The change in surface area of the material is vital from the gas sensing application point of view. The detailed characterizations i.e. XRD, XPS etc. of all the synthesized nanoheterostructures needs to be carried out.
In the present study the samples prepared under 10^{-4} mbar air pressure with 80 A of filament current and 30 minutes of deposition time, because of the satisfactory growth of WO_x wires forming heterostructure, were used for further characterization and gas sensing applications.

### 2.3.3 XRD

The presence of several sharp peaks in XRD pattern indicates that the samples are of polycrystalline nature. The peaks in the XRD pattern are identified by using JCPDS data. The SnO_2 is present in rutile phase with the parameters a = 4.74 and c = 3.1885 Å and W_{18}O_{49} is present in the monoclinic form with the lattice constants with a = 18.33, b = 3.786, c = 14.04 Å [42]. It is confirmed that the sample exists in two distinct phases that are of pure SnO_2 and WO_x respectively and absence of mixed or alloy phases such as tin tungstate. This is the conclusion from XRD result only. There is detection limit for XRD and there can be mixed phases at the interface between SnO_2 and WO_x. Therefore further study is carried out by using HRTEM.
2.3.4 XPS (X-ray Photoelectron spectroscopy)

XPS spectra of the sample are presented in Figure 2.8. Calibration with respect to binding energies of Au 4F$_{7/2}$ is carried out. The binding energies at 486 eV and 494 eV are of Sn - 3d$_{5/2}$ and 3d$_{3/2}$ states corresponding to Sn$^{4+}$ states in SnO$_2$.

![XPS spectra of SnO$_2$-WO$_x$ hierarchical nanoheterostructures.](image)

This confirms that the samples are of stoichiometric SnO$_2$ nanowires. The XPS of W shows a broad spectrum of binding energies. The spectrum is deconvoluted into six peaks corresponding to binding energies of WO$_x$. This confirms that W exists in multiple oxidation states corresponding to W$^{6+}$, W$^{5+}$ and W$^{4+}$ as reported in some earlier studies [35, 39] and presence of the oxygen deficient phase of tungsten oxide. The O1s spectrum has
been de-convoluted 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 present on the surface of the samples.

2.3.5 Uv-Vis absorption spectra

Figure 2.9 Uv-Vis absorption spectra of SnO₂-WOₓ hierarchical heterostructures in the inset. spectrum plotted as (α hν)^2 versus energy.

The optical properties of a material are important as they provide information on electronic band structures, band states, defects and type of optical transition therefore we have investigated the Uv-Vis spectra of hierarchical heterostructures.
The Uv-Vis absorption of the hierarchical heterostructures shows two absorption wavelengths. Frequency dependence of absorption coefficient of semiconductors is given by

\[ \alpha (\nu)h\nu = A(h\nu - E_g)^{m/2} \]

Where, \( \alpha \) is the absorption coefficient, \( \nu \) is the frequency of photons, \( A \) is constant and \( m \) is 1 for direct transition. To determine band gap \( (E_g) \) we have plotted \((\alpha h\nu)^2\) as a function of \( h\nu \) Figure 2.9. The straight line fit yields the optical band gap. One peak corresponding to SnO\(_2\) at 340 nm (Figure 2.9) as the edge of spectrum of Uv-Vis and one small peak at 404 nm. It is found that the band gap for SnO\(_2\) is 3.6 eV and for WO\(_x\) is 2.5 eV. The band gaps are different for two different materials. If the material would have been in the form of alloy a single peak in between the two phases would have been obtained. As the band gap is changed there must be electronic interaction between the metal oxides. Further study is needed to understand the junction properties and the defect states getting created in the sample. The edge or the line of contact between the two components in the hierarchical nanoheterostructures is studied by using HRTEM measurements.

### 2.3.6 HRTEM

HRTEM samples were prepared by dispersing the SnO\(_2\)-WO\(_x\) heterostructures into ethanol. A dilute solution was prepared. A drop of the solution was put on the carbon coated Cu grid especially meant for TEM study. The sample was kept for sometime to let the ethanol evaporate and used for TEM analysis.
Figure 2.10 TEM image of the sample a) SnO$_2$-WO$_x$ hierarchical heterostructures b) HRTEM image at the junction.

From the TEM images it is observed that on the surface of SnO$_2$ nanowire (diameter about 100 nm) the WO$_x$ nanowires are grown with length of about 1-2 $\mu$m and the diameter less than 50 nm. Figure 2.10 b) HRTEM confirms that there are two distinct phases of SnO$_2$ and W$_{18}$O$_{49}$ present with the interplanar spacing of 0.33 nm and 0.29 nm, respectively. Presence of any other mixed or alloy phases could not be detected in the samples.

2.4 Gas sensing Study

The peculiar structural and morphological properties of hierarchical heterostructures of metal oxide nanowires are suitable for the development of novel devices and in particular gas sensors. The sensing mechanism underlying the semiconducting metal oxides relies on redox reactions occurring between gaseous molecules and active ions such as OH$^-$, O$_2^-$, O$^-$ adsorbed over the metal oxide surface depending on its temperature [40].
Such redox reactions modulate the surface population of the above active ions and thus the space charge layer depth within the metal oxide.

In this particular study a comparative analysis of the sensing between pure SnO$_2$ mat films, the single wire films of SnO$_2$-WO$_x$, SnO$_2$-WO$_x$ mat films and WO$_x$ thin films is presented. The films made are viz. as under a) pure SnO$_2$ mat films, b) SnO$_2$-WO$_x$ single wire films c) SnO$_2$-WO$_x$ mat films and d) WO$_x$ thin films. In Figure 2.12 a) comparison between the mat type films is presented for 8 ppm concentration of H$_2$S and Cl$_2$ gas.

### 2.4.1 Mat film

The gases employed in the study are (H$_2$S- reducing gas) and Cl$_2$ (oxidizing gas). The response of the films in the presence of two gases is usual i.e. resistance decreases when exposed to H$_2$S and it increases when exposed to Cl$_2$ gas. (Shown deliberately in terms of current in Figure 2.12 c) and d)

The response is defined as the ratio of resistance of the film in presence and absence of gas ($R_g/R_a$) for Chlorine gas (oxidizing gas) and ($R_a/R_g$) for H$_2$S (reducing gas). The sensitivity is about 30 times for H$_2$S gas and about 2 times in presence of Cl$_2$ for 8 ppm concentration for SnO$_2$ pure mat films.
(Figure 2.12 a),b)). Whereas in case of SnO$_2$-WO$_X$ films the sensitivity is 3 times and about 10 times for 8 ppm concentration of H$_2$S and Cl$_2$ gas respectively (Figure 2.12 c) and d)). The sensitivity curves are plotted in terms of current in order to show that the films are showing normal response to oxidizing and reducing gases. These results confirm that the film is getting selective for Cl$_2$ gas. The sensitivity of WO$_X$ thin film is presented (Figure 2.12 e) and f)). The films of WO$_X$ show less sensitivity for 20 ppm H$_2$S. In presence of Cl$_2$ gas the resistance of the film increases however it recovers very slowly which is obvious at room temperature. This confirms that the SnO$_2$- WO$_X$ mat films give considerably better results and the heterostructures can be used for sensor applications.
Figure 2.12 Response of mat type sensor films at room temperature on exposure to 8 ppm concentration gas. Pure SnO\textsubscript{2} films exposed to a) H\textsubscript{2}S and b) Cl\textsubscript{2}. SnO\textsubscript{2}/WO\textsubscript{x} heterostructures films exposed to c) H\textsubscript{2}S and d) Cl\textsubscript{2}. WO\textsubscript{x} films exposed to e) 20 ppm H\textsubscript{2}S gas f) 1 ppm Cl\textsubscript{2} gas.
2.4.2 Single wire

The response of SnO₂ pure and SnO₂-WOₓ mat films is as usual for reducing (H₂S) and oxidizing gases (Cl₂); in case of single wire of SnO₂-WOₓ however, it is observed that the response is proper to reducing gas such as H₂S but anomalous in case of Cl₂. For single wires of SnO₂-WOₓ, the resistance of the film decreases with the exposure to oxidizing (Cl₂) gas. The response time is within the range of seconds and recovery is in minutes. It goes on increasing at higher concentrations which is obvious at room temperature. The lower limit (lowest measurement possible) is 0.5 ppm of Cl₂ gas (Figure 2.13a). The anomalous behavior explained as

Figure 2.13 Current as a function of time for single wire SnO₂/WOₓ heterostructure sensor on exposure to a) 0.5 ppm b) various concentrations of Cl₂ gas at room temperature.
The response of polycrystalline sensors generally has two distinct contributions i.e. from intra grain regions and grain boundaries. Single wire sensors have only intra grain contributions while the mat type films have intra grain as well as grain boundary contributions. From the above results of our mat film and single wire responses it is observed that the grain boundary contributions show normal response however the intra grain contribution show anomalous response to Cl₂ gas. The mechanism proposed in ref 42 is for interaction of Chlorine gas with all kinds of metal oxide systems and thus is suitable in our system also. Further our nanowires are single crystalline in nature as supported by the TEM. It may be mentioned that nanowires for different materials reported in literature by similar techniques are normally crystalline.

Four different reactions of Chlorine with semiconductor oxides have been reported. As shown

\[ \frac{1}{2} \text{Cl}_2 + \text{O}^{2-}_{(ad)} \rightarrow \text{Cl}^-_{(ad)} + \frac{1}{2} \text{O}_2 + e^- \]  
\[ \text{(1)} \]

\[ \frac{1}{2} \text{Cl}_2 + \text{O}^{2-}_{(ad)} \rightarrow \text{Cl}^-_{(ad)} + \frac{1}{2} \text{O}_2 + e^- \]  
\[ \text{(2)} \]

\[ \frac{1}{2} \text{Cl}_2 + e^- \rightarrow \text{Cl}^-_{(ad)} \]  
\[ \text{(3)} \]

\[ \frac{1}{2} \text{Cl}_2 + e^- + V_0 \rightarrow \text{Cl}^-_0 \]  
\[ \text{(4)} \]

The terms in the bracket (ad) represent species adsorbed on the surface of semiconductor oxide particles and O represent the species occupying lattice site oxygen and V₀ indicates vacancy at the 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 the
surface or at oxygen vacancy site yield normal response with resistance increasing on exposure to Chlorine. Results indicate that in case of single wire which is polycrystalline, 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 case of mat type sensor, there are a large number of defect sites between the grains on which additional chlorine may be adsorbed leading to normal response to chlorine with increase in resistance.

### 2.5 Discussion

The synthesis of SnO$_2$-WO$_x$ hierarchical nanowires heterostructures is discussed first, the results obtained basically through the usage of a separate deposition systems. A single- crystalline nanowire grown by direct vapor solid growth (SnO$_2$ nanowire) acts as a backbone for the second condensation step, in which polycrystalline nanograins (WO$_x$) completely cover the backbone. The disorder structures during the formation of SnO$_2$ nanowires act as the site for the growth of WO$_x$ nanowire structures. In these conditions the synthesis leads to anisotropic growth of a longitudinal heterostructures. In this way radial heterostructures can be fabricated without adding any catalyst [41].

Based on all the possible reactions at the filament and the template (SnO$_2$ nanowire Figure 2.6), a nucleation and growth model as shown in Figure 2.14 is proposed for the observed 1-D growth of tungsten oxide nanowires.
The high supersaturation of WO$_2$ (gas) leads to condensation into WO$_2$ (solid) clusters in a nucleation step. Further oxidation of WO$_2$ clusters could be favorable at the crystal-template interface, which leads to precipitation of WO$_{3-x}$ crystals on the template (SnO$_2$ nanowire) with a tip whose dimensions are considerably less than the crystal. 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 [37] where the growth occurs by nucleation of WO$_2$ clusters followed by precipitation of WO$_{3-x}$ crystals having tip of considerably smaller dimensions. Enhanced adsorption of WO$_2$/WO$_3$ species on the tip was proposed to result in the growth of nanowires. Partial pressure of oxygen (in $10^{-5}$-$10^{-3}$ mbar range) employed in present study is much less than 0.1-10 mbar used by Thangala et al [37] and this may help in nucleation of oxygen deficient WO$_2$ nuclei.

Hence there was no tip associated with the tungsten oxide nanowires and the entire nanowire was composed of one phase that is the oxygen deficient W$_{18}$O$_{49}$ phase.

The gas concentration is measured as follows: 500 ml of 1000 ppm concentrated 99 % pure gas (Balance nitrogen) cylinders were purchased from chemtron company Mumbai. 10 ml of it when taken in a syringe then that contains 1000 ppm of the desired gas; when it is allowed in the 250 ml container containing the film the gas concentration in the container is 40 ppm of the desired gas.
High sensitivity to Chlorine and reduced sensitivity to H₂S for single wire sensors can be explained with respect to SnO₂-WOₓ band diagram shown in Figure 2.15. Typical values of electron affinity and work function of WOₓ and SnO₂ has been taken from the literature. It is seen that the electron density is enhanced in SnO₂ near the junction while it is reduced in WOₓ. The width of region with enhanced electron density (region marked as A in Figure 2.15) near junction in SnO₂ is expected to cover nearly full nanowires cross section.

In single wire sensors the conduction takes place through SnO₂ wire as WOₓ wires forming branches on SnO₂ stem are not connected to each other. From band diagram (Figure 2.15a) it is observed that the electrons in WOₓ are at higher energy than those in SnO₂. Response to Chlorine occurs in reactions 1 and 2 taking place in WOₓ and SnO₂. As the electrons generated in WOₓ are transferred to SnO₂, a larger change in resistance of SnO₂ nanowire occurs that would take place in case of pure SnO₂ nanowire. To understand reduced sensitivity to H₂S we note that air resistance of the hetero junction is reduced in comparison to pure SnO₂ (Figure 2.15b). Interaction of WOₓ nanowires with the H₂S is low as WOₓ are already oxygen deficient and not very good sensor to H₂S. Better response to chlorine and lower response to H₂S explain improved selectivity of single wire hetero-junction sensor.
Figure 2.15 Band diagram (a) isolated W18O49 and SnO2 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 _. Region A has enhanced electron density in SnO2 and region B has reduced electron density in W18O49. Region A with enhanced electron density may cover full nanowires as typical depletion layer width exceeds nanowire thickness.

2.6 Conclusion

We have shown how controlled nanoheterostructures can be formed by a simple two step thermal evaporation technique. Concerning gas sensing applications hierarchical metal oxide (SnO2-WOx) nano heterostructures demonstrate a high sensitivity to gases such as H2S and Cl2. The
functional tests performed on single wires show interesting results for the
detection of Cl₂ with detection limit upto 0.5 ppm level and relatively fast
response and recovery times. Greater surface to volume ratio, better
stoichiometry and greater degree of crystallinity compared to
polycrystalline oxides, reduced instability make these materials promising
for the development of a new generation of sensors.

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