# Growth and gas-sensing studies of metal oxide semiconductor nanostructures

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**Abstract:** One-dimensional (1D) nanostructures of semiconductor oxides are of interest for various applications including gas sensors. For gas sensors, nanostructures have advantages of improved gas-sensing characteristics and have potential in fabrication of miniature sensor. In this paper, we review some of the work done in our laboratory towards growth of nanostructures of SnO<sub>2</sub>, ZnO and CuO and hierarchical nano-heterostructures of CuO:W<sub>18</sub>O<sub>49</sub>, SnO<sub>2</sub>: W<sub>18</sub>O<sub>49</sub> and ZnO:W<sub>18</sub>O<sub>49</sub> as well as investigation of their gas-sensing properties. All nanostructures except CuO have been prepared by thermal evaporation technique. CuO nanowires have been grown by thermal oxidation of copper foils under oxygen atmosphere. Gas sensing has been investigated in

- isolated 1D structures placed between two electrodes
- films prepared from their suspension in organic solvents or direct growth of nanostructured films on substrates.

The results show that isolated 1D nanostructures of pure  $SnO_2$  and ZnO are highly sensitive for room temperature detection of  $H_2S$  and NO gases respectively while  $SnO_2$ : $W_{18}O_{49}$  heterostructures may be used for the detection of chlorine.

Keywords: nanowires; gas-sensing properties; thin films; isolated 1-D nanostructures.

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#### 1 Introduction

Nanostructures have received steadily growing interest because of their fascinating properties as compared to their bulk or microsized counterparts. In recent years, one-dimensional (1D) nanostructures (of different materials) such as nanowires, nanobelts, nanorods and nanotubes have been focus of intensive research for various device applications. In particular, metal oxides nanostructures have been of interest for applications such as heterogeneous catalysts [1], dye sensitised solar cells [2], optoelectronics and gas sensors [3]. They are advantageous for gas sensing as they enable miniaturisation of sensor size, reduced power requirement and better gas-sensing characteristics due to increased surface to volume ratio.

Broadly, there are two different approaches to the production of 1D nanostructures. These are top-down and bottom-up processes. In top-down approach, nanostructures may be obtained [4,5] by starting from bulk material and reducing the size by various lithography techniques. This technology has relatively high cost and it is difficult to prepare large number of devices by this technique. Some of the other top-down techniques are attrition or ball milling. Generally these methods lead to materials with defects. Bottom-up approach refers to building nanoparticles atom-by-atom or molecule-by-molecule and various natural biological processes result in growth of materials by this method. Various techniques in this category are electrochemical deposition, solution-based techniques [6,7], heating of bulk material and physical vapour deposition. Material prepared by physical method is preferred as it has high purity due to absence of solvents, has better crystallinity due to higher temperatures and has the possibility of doping and preparation of heterostructures.

Many of the metal oxides semiconductors (and some non-oxide materials such as tellurium and polymers) and their nanostructures have been widely employed for gas-sensing applications [8]. Oxide semiconductors sense gases by their interaction with adsorbed oxygen on the surface. Adsorbed oxygen traps electrons from bulk of semiconductor and interaction with various reducing ( $H_2S$ ,  $NH_3$ ,  $H_2$  etc.) and oxidising gases (NO, O<sub>3</sub>) results in change in concentration of trapping centres (adsorbed oxygen). This in turn yields change in conductivity that is a measure of gas concentration. The main drawback of most of semiconductor sensors is their lack of selectivity. This problem has been addressed by doping with other elements or metal oxides. For example, doping of CuO into  $SnO_2$  is known to enhance its selectivity (as well sensitivity) towards detection of H<sub>2</sub>S gas [9-11]. Reported explanation for this enhanced sensitivity and selectivity depends on the formation of p-n junctions between the SnO<sub>2</sub> (n-type material) and CuO (p-type material) grains that result in very high resistance (due to random reverse biased junctions) of the films in air. H<sub>2</sub>S gas reacts with CuO forming CuS (that is metallic in nature). Consequently p-n junctions break down yielding a large decrease in the resistance of the films. Due to specific interaction of  $H_2S$  with

CuO high selectivity is obtained. Another method of improvement in selectivity is by use of suitable microstructure as will be shown by our studies.

Nanostructures may result in improved sensor characteristics due to

- increased surface area to volume ratio yielding better sensitivity
- higher reactivity of nanomaterials due to defects at surfaces that often results in room temperature operation [12–14].

Further, it may be possible to dope nanostructured materials with elements that are difficult to dope in bulk as will be shown by doping of  $SnO_2$  nanowires by CuO. An area of research that has not been much explored is fabrication of hierarchical nano-heterostructures with built-in heterojunctions that provides a way for tailoring materials with better gas-sensing properties [15–17]. As an effort in this direction, Chen et al. [18] have shown highly selective sensing of ethanol by heterojunction barrier controlled mechanism using  $SnO_2/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical nanostructures.

In this paper, we review some of the work done in our laboratory towards growth of nanostructures of  $SnO_2$ , ZnO and CuO and hierarchical nano-heterostructures of  $CuO:W_{18}O_{49}$ ,  $SnO_2:W_{18}O_{49}$  and  $ZnO:W_{18}O_{49}$ . Gas-sensing characteristics have been investigated using:

- isolated 1D structures such as nanowires placed between two electrodes
- films prepared from their suspension in organic solvents or direct deposition on substrates.

These studies show significant difference in gas-sensing characteristics of bulk and interface regions and provide a way for improving selectivity for some gases by suitably tailoring the microstructure. We have divided this review in two parts experimental and results and discussion. In experimental part we describe growth of nanowires, give details of various systems used, describe fabrication of sensors with different configurations and gas-sensing properties of various nanowires. In Section 1 we discuss about SnO<sub>2</sub> and SnO<sub>2</sub>:CuO nanowires, in Section 2 we describe gas-sensing properties of CuO nanowires in different configuration and in Section 3 we discuss gas-sensing properties of znO nanowires. In Section 4 we describe growth and gas-sensing properties of various heterostructure nanowires.

#### 2 Experimental

Growth of nanostructures was carried out by thermal evaporation of metal or metal oxides at atmospheric pressure or under high vacuum conditions. The set up used for growth at atmospheric pressure is shown in Figure 1. The system consists of a tubular furnace in which a quartz tube was placed for growth of materials. Source material (metal or metal oxides with graphite) was placed in a boat in high temperature zone of the furnace. Gas flow rate and fraction of oxygen and argon over the source could be controlled by using flow meters. Source temperature and heating and cooling rates were controlled by a Eurotherm make temperature controller. Profile of the furnace at source temperature of 1050°C is shown in Figure 1. In different experiments, nanostructures were obtained at source itself or (downstream) at different temperatures in

the gas flow direction as the temperature gradient provides suitable conditions for condensation and nucleation of the nanostructures. Detailed growth conditions for each material will be given later. Growth under vacuum was carried out using a conventional thin film deposition system with ultimate vacuum of  $10^{-6}$  torr and oxygen pressure controlled using a needle valve.

Figure 1 Schematic diagram of the experimental set up used for growth of nanostructures at atmospheric pressure. Lower figure shows temperature profile along the length of quartz tube



Nanostructures were characterised for morphology and structure by various techniques. Surface morphology of the samples was studied by scanning electron microscopy (SEM) carried out using TESCAN make VEGA MV2300T/40 system. Length and diameter of nanowires were determined from SEM images and chemical state of elements was studied by X-ray photoelectron spectroscopy (XPS). XPS was carried out using Mg-K $\alpha$ (1253.6 eV) source in RIBER make system comprising a twin anode X-ray source and a MAC-2 electron analyser. The binding energy scale was calibrated in few cases to C-1s line at 285 eV and in a few cases to Au-4f line at 84 eV. Energy dispersive X-ray analysis (EDAX) was carried out to determine the chemical composition. The crystal structure and nature of chemical phases were investigated by X-ray diffraction (XRD) measurements carried out using Cu-K $\alpha$  radiation. In some cases, the morphology of the nanowires was also observed by transmission electron microscopy (TEM) carried out using a JEOL 2000 FX electron microscope. Band gap of the prepared structures was determined from absorption spectra obtained by using a UV-Vis spectrophotometer (Chemito model spectroscan UV 2600). The spectra were analysed to determine the band gap by fitting of the data to the following equation:

$$\alpha(v)hv = A(hv - E_{\sigma})^{m/2} \tag{1}$$

where,  $\alpha$  is the absorption coefficient,  $\nu$  is the frequency of photons, A is a constant and m = 1 and 4, for direct allowed and indirect allowed transitions respectively.

Various nanostructures were investigated for change in the conductance on exposure to oxidising and reducing gases to assess their suitability as gas sensors. For this purpose, two types of sensors were fabricated and these are discussed below.

- *Nanostructure films*: For preparation of films of nanostructures on alumina substrates, two gold contacts with desired spacing were first deposited by thermal evaporation technique. Silver wires were attached to these contacts for measurement of resistance using simple two-probe technique. Films of nanostructures as nanoparticles or nanowires or tetrapods could be deposited on these substrates by dispersion of nanostructures in organic solvents such as methanol and then placing few drops of this suspension on the substrates. In some cases, the deposited films were annealed at temperatures up to 500°C to improve contacts between nanostructures. SEM of a typical sensor prepared in this manner is shown in Figure 2(a). Some films were also prepared by direct (thermal) deposition of nanostructures on alumina substrates. Resistance of these films has contribution from intragrain region of nanostructures and due to grain boundaries. As will be shown later, the response of these regions to gases is significantly different.
- Isolated 1D nanostructures: In the second type of sensors one or few 1D nanostructures such as nanowires or nanobelts were aligned between two gold contacts and their resistance was measured by two-probe technique. As there are no grain boundaries, the response of these sensors depends on conductance change of intragrain regions only. Electrical contacts to isolated nanowires were made in two different ways. In the first technique, an optical microscope was used. Here, a drop of very dilute dispersion of nanowires (in organic solvent) was placed on the substrate. Single nanowire was chosen by use of microscope. The observation and separation of single nanowires by optical microscope was aided by organic solvent sticking to nanowires by surface tension increasing its size. A metal mask with 12-25 µm spacing (created using metal wires of same diameter) was aligned to nanowires. Subsequently, gold contacts were deposited by thermal evaporation technique. This method is suitable for very long nanowires with length exceeding about 100 µm as small length wires are difficult to identify. A single SnO<sub>2</sub> nanowire isolated by this technique is shown in Figure 2(b). In the second method, dielectrophoresis technique was used to align isolated nanowires between two pre-deposited gold electrodes having desired spacing (10–25  $\mu$ m range). For this purpose, a large number of contacts with required spacing were deposited on a substrate and an ac electric field (~20 V at 100 kHz) was applied between each set of gold electrodes [19]. Nanowires with very small concentration were dispersed in methanol and were deposited dropwise between the gold contacts. Each drop was allowed to dry under applied field before putting the next drop. The substrates were then viewed under SEM to identify sets of electrodes with one or few nanostructures aligned between them. SEM of a sample with two ZnO nanowires is shown in Figure 2(c).

For measurement of the response to gases, a miniature Pt heater cum temperature sensor was attached to the backside of the sensor and the same was fixed in a stainless steel housing (see Figure 3) with a temperature controller circuit. The sensor housing was loaded in a container having a volume of  $250 \text{ cm}^3$  [20] and the temperature of the film was set to desired value. Toxic gases having 1000 ppm concentration (obtained in half litre cylinders) were used for measurements. Measured quantity of desired gas was introduced in the housing (through a neoprene gasket) using a syringe, so as to yield the desired concentration (typically in 0.1–200 ppm range) of gas and resistance

of the film was measured as function of time. The data was acquired by using a personal computer. After steady state was achieved, recovery of sensors was studied by opening the housing to the atmosphere.

**Figure 2** SEM micrographs of (a) thin film type sensors (b) single SnO<sub>2</sub> nanowire aligned between two gold electrodes using optical microscope and (c) two ZnO nanowires aligned between gold contacts using dielectrophoresis technique (see online version for colours)





Figure 3 Schematic diagram of experimental set up used for measurement of response of sensors to different gases (see online version for colours)



Response (S) of sensors to different gases was calculated using the relation:

$$S = R_g / R_a \tag{2}$$

where,  $R_a$  and  $R_g$  are resistances in air and gas respectively. Response and recovery times were defined as time needed for 90% of total resistance change on exposure to gas and air respectively. In some of the discussion, sensitivity defined as  $R_g/R_a$  (for increase in resistance on exposure) or  $R_a/R_g$  (for decrease in resistance on exposure) has been used.

#### **3** Results and discussion

Growth and gas-sensing properties of nanowires are described in the following section. This study highlights the difference in gas-sensing properties of same kind of nanowires in different configurations.

## 3.1 SnO<sub>2</sub> and SnO<sub>2</sub>:CuO

Growth of pure and copper doped  $SnO_2$  nanowires is important as  $SnO_2$  is the most important oxide semiconductor sensor material and copper doping is known to yield highly sensitive and selective H<sub>2</sub>S sensors via formation of random p-n junctions as Cu does not dissolve in SnO<sub>2</sub> matrix in bulk material. Growth of pure SnO<sub>2</sub> nanowires was carried out by thermal evaporation at atmospheric pressure using high purity Sn powder as source. The powder was placed in an alumina boat, the furnace temperature was increased to 900°C in the presence of Ar gas (with ~0.1% oxygen) and maintained there for 1 h. Growth of nanowires/belts was observed on the top of the alumina boat as white wool like material (Figure 4). For growth of Cu doped SnO<sub>2</sub> (SnO<sub>2</sub>:CuO) nanowires, Cu powder (0-50% by weight) was mixed with Sn powder in the initial charge. In the following, samples prepared with 0, 5, 16 and 50% copper in the starting charge have been named as Cu0, Cu5, Cu16 and Cu50 respectively. The nanowires were found to nucleate on the walls of the alumina boat and grow towards the centre. The nanowires growth in this case has been attributed to vapour solid growth mechanism [21]. Typical SEM micrographs of pure SnO<sub>2</sub> (Cu0) and Cu5 nanowires are shown in Figure 5. The samples consist of nanowires and nanobelts with diameter of nanowires and thickness of nanobelts in 50-150 nm range. In what follows we sometime refer to nanobelt/nanowire combination as nanowires. It is seen that the diameter of nanowires reduces as copper content increases [21]. This could be due to increased stress in the lattice in copper doped samples or reduced vapour pressure on addition of copper [22]. EDX analysis showed that the atomic fraction of Cu varies from  $\sim 2\%$  to  $\sim 2.5\%$  when weight of Cu in starting mixture increases from 5% to 50%. This indicates that Cu is doped in SnO<sub>2</sub> nanowires and its content is limited by its solubility.

Results of XRD and optical absorption studies further showed that Cu is doped in the nanowire lattice. XRD (some typical spectra shown in Figure 6(a)) showed systematic reduction in lattice parameters (*a* and *c* reduced from 4.74 Å and 3.188 Å for Cu0 samples to 4.73 Å and 3.187 Å respectively for Cu16 samples) as copper content in starting charge increased. Further, no peaks pertaining to Cu or CuO were observed. Lattice parameters reduction is attributed to smaller size of Cu ion (0.57 Å) compared to that of Sn ion (0.69 Å). Typical UV-Visible absorption spectrum of nanowires dispersed

in ethanol solution plotted as  $(\alpha h v)^2$  vs. hv is shown in Figure 6(b). Using equation (1) for direct band gap materials, the intercept of these plots gives band gap. It is seen that the band gap systematically reduces as copper content in initial charge increases. The systematic changes in lattice constants and band gap show that copper is doped in SnO<sub>2</sub> lattice when the material is in nanowire form. This result is in contrast to those reported on thin films and bulk SnO<sub>2</sub>:CuO samples where CuO is found to precipitate out of SnO<sub>2</sub> matrix [23]. These results indicate that conventional p-n junction mechanism of H<sub>2</sub>S gas sensing by SnO<sub>2</sub>:CuO is not possible for these nanowires. We may add that similar decrease in the band gap of SnO<sub>2</sub> has been reported for doping with other transition metals as Zn, Mn and Co etc. [24–26].

Figure 4 Optical photograph of alumina boat with  $SnO_2$  nanowires. White nanowires are seen to grow from edges of the boat. Black material at the bottom of the boat is un-reacted source powder (see online version for colours)



Figure 5 SEM micrographs of SnO<sub>2</sub> nanowire samples: (a) undoped (Cu0) and (b) 5% copper doped (Cu5) (see online version for colours)



Gas-sensing characteristics were studied for film and single wire sensors prepared using pure and doped  $SnO_2$  nanowires. Both types of sensors (made using undoped Cu0 nanowires) were found to be quite sensitive to  $H_2S$  and chlorine gases at room temperature. Typical response curves for these two gases plotted as conductance vs. time are shown in Figure 7. The results show that

- sensitivity is significantly higher for single wire sensors
- the change in resistance on exposure to chlorine gas is opposite for films and single wires.

While the response for films is in the expected direction (chlorine being oxidising gas, an increase in resistance is expected as absorbed gas will trap electrons leading to increase in resistance for  $SnO_2$ , a n-type material), that for single wires is anomalous. In the case of films, both intragrain and grain boundaries contribute to resistance and in case of single wires, grain boundaries are absent. The results indicate significantly different response of intragrain and grain boundary regions. Anomalous response of single wire sensors (to chlorine) may be explained in the following manner. Four different interactions of chlorine with semiconductor oxides have been reported [27].

$$\frac{1}{2}\text{Cl}_{2} + \text{O}_{(\text{ad})}^{2-} \to \text{Cl}_{(\text{ad})}^{-} + \frac{1}{2}\text{O}_{2} + e^{-}$$
(3)

$$\frac{1}{2}Cl_2 + O_0^{2-} \to Cl_0^{-} + \frac{1}{2}O_2 + e^{-}$$
(4)

$$\frac{1}{2}\mathrm{Cl}_{2} + \mathrm{e}^{-} \to \mathrm{Cl}_{(\mathrm{ad})}^{-} \tag{5}$$

$$\frac{1}{2}\mathrm{Cl}_{2} + \mathrm{e}^{-} + \mathrm{V}_{\mathrm{o}} \to \mathrm{Cl}_{\mathrm{o}}^{-} \tag{6}$$

where, subscripts (ad) and O indicate species adsorbed on surface of semiconductor oxide particles and species occupying oxygen lattice site respectively and  $V_O$  indicates vacancy at oxygen site. Reactions 3 and 4, where chlorine replaces lattice or adsorbed oxygen, result in anomalous response while reactions 5 and 6, where chlorine is adsorbed at surface or at oxygen vacancy site, yield normal response expected from oxidising gases. In crystalline single nanowires, reaction predominantly occurs with lattice oxygen and oxygen adsorbed on surface as additional sites for chlorine adsorption are not available due to low defect density. For film type sensors, additional chlorine may be adsorbed on defect sites between the grains resulting in expected (normal) response.

Figure 6 (a) XRD spectra of Cu0, Cu5 and Cu16 nanowire samples and (b) corresponding optical absorption spectra







Sensitivity of films type sensors (for  $H_2S$  gas) was seen to increase while that of single wire sensors was found to decrease with increase in temperature (data not shown here). Therefore, further measurements on single wires have been carried out at room temperatures and those on films at 150°C. Effect of doping on response of single wire and film type sensors was studied and the response of Cu0 and Cu5 type sensors has been compared in Figure 8. It is seen that on Cu doping, the sensitivity of films increases while that of single wires reduces, further demonstrating the quite significant difference in contributions of intragrain and grain boundary regions. For Cu16 films, a sensitivity of  $6 \times 10^6$  on exposure to 50 ppm of H<sub>2</sub>S was observed at 150°C [21]. This is possibly the highest value of sensitivity reported for SnO2:CuO based sensors. The high value of response of copper doped nanofilms (where no p-n junctions are formed) indicates that the reported p-n junction mechanism of high response in bulk of SnO<sub>2</sub>:CuO may not be complete. The high response in present study is attributed to large changes in barrier heights of grain boundaries in copper doped films on exposure to H<sub>2</sub>S. Further studies are needed to understand why such changes in Cu doped films are larger. High response of copper doped films at high temperatures (compared to single wires) indicates that it arises predominantly from changes in resistance of grain boundaries. This was confirmed by Kumar et al. [21] using impedance spectroscopy studies on the films.

**Figure 8** Comparison of response (*S*) of sensors prepared using pure (Cu0) and 5% copper doped (Cu5) SnO<sub>2</sub> nanowires on exposure to H<sub>2</sub>S gas: (a) single nanowire sensors tested at room temperature and (b) film type sensors tested at 150°C



#### 3.2 CuO nanowires

Growth and gas sensor study on CuO nanowires was taken up as it is a p-type semiconductor in contrast to most of other oxide semiconductors (that are n-type). The growth of these nanowires was carried out by thermal oxidation of high-purity Cu sheets of 1 mm thickness under flowing oxygen. Thermal oxidation was carried out at atmospheric pressure at different temperatures (between 400°C and 700°C) and times up to 48 hr [28] with a heating rate of 6°C/min. Results of SEM studies carried out on samples prepared at different temperatures (for 2 h) are shown in Figure 9. Optimum growth was found to be in temperature range of 650-675°C (SEM of 675°C samples not shown here). At high temperatures (700°C), thickness of the wires increases and length decreases. The length of nanowires was found to increase with time and as shown in Figure 10(a), nanowires with length of  $\sim$ 50 µm could be grown in 24 hrs at temperature of 675°C. Diameter of nanowires at 675°C is found to be in the range of 50-200 nm. XRD spectra (shown in Figure 10(b)) confirmed nanowires to be CuO. Small peaks due to Cu<sub>2</sub>O were found to arise from its presence at interface between Cu sheet and nanowires. This was confirmed by recording XRD spectra after scrapping the nanowires (data not shown here) whereby peaks corresponding to Cu<sub>2</sub>O increased. Formation of Cu<sub>2</sub>O during growth of nanowires has also been reported in other studies [29]. XPS spectra (Figure 11) also confirmed the nanowires to be CuO. For comparison, CuO thin films were also grown by thermal evaporation of copper followed by oxidation to 600°C. SEM of a typical film is shown in Figure 9(f). The films are granular with grain size of  $5-10 \,\mu\text{m}$ .

Figure 9 SEM images of CuO nanowires prepared by heating Copper sheet under oxygen atmosphere (for two hours) at different temperatures of (a) 400°C, (b) 500°C, (c) 600°C, (d) 650°C, (e) 700°C. Figure (f) shows SEM of a CuO thin film (see online version for colours)



#### Growth and gas-sensing studies



(see online version for colours)



Figure 11 XPS spectra of CuO nanowires showing formation of CuO



For the determination of band gap, UV–Visible absorption spectrum of CuO nanowires dispersed in methanol solution was recorded. The band gap of CuO nanowires was calculated by extrapolation of  $(\alpha h v)^2$  vs. hv plot as shown in Figure 12. The band gap for nanowires (2.03 eV) was found to be larger than that reported for bulk CuO (1.85 eV). Larger value of band gap for nanowires is in agreement with other studies [30]. Growth of nanowires by thermal oxidation of copper sheets is attributed to relaxation of stresses generated during oxidation of copper. High rate of oxidation coupled with low mobility in solid state leads to stress in the copper sheets that is released by formation of small CuO crystallites from which the wires grow [28]. As reported earlier, support for this growth mechanism is provided by

- formation of hill and valley structure as well as CuO crystallites observed at the base of nanowires [28]
- no nanowires grow from polycrystalline Cu<sub>2</sub>O pellets though Cu<sub>2</sub>O formation at the interface occurs before growth of nanowires from copper sheets [28].

CuO nanowires were investigated for response to different gases. Unlike many n-type semiconductors such as ZnO,  $SnO_2$  and  $In_2O_3$ , not many studies have been reported

for gas-sensing behaviour of p-type oxides and therefore it is of interest to study interaction of CuO with gases. Three different types of CuO samples were studied

- as grown CuO flakes with nanowires
- isolated nanowires aligned between two electrodes
- CuO thin films prepared by thermal evaporation.

**Figure 12** Absorption spectra of CuO nanowires plotted as  $(\alpha h v)^2$  vs. hv. Inset shows absorbance as function of wavelength (see online version for colours)



Gold contacts were deposited on as-grown CuO flakes (with nanowires) and effect of exposure to different gases such as H<sub>2</sub>S, NH<sub>3</sub>, NO, CO and CH<sub>4</sub> was studied. At room temperature, the flakes showed good response to  $H_2S$  gas (Figure 13(a)) and very small response to NO, inset of Figure 13(a). However, the response to H<sub>2</sub>S consisted of increase in resistance followed by decrease. The recovery was quite slow at 10 ppm and incomplete on exposure to higher concentration of 50 ppm (inset of Figure 13(a)). At higher operating temperatures (Figure 13(b)), resistance was seen to predominantly reduce (with very small initial increase) while the recovery was complete though recovery time tended to be large at high concentrations (recovery time ~1000 s at 10 ppm). To understand complex behaviour of response to  $H_2S$ , we carried out XPS measurements after exposure at high concentration (250 ppm) and the results are shown in Figure 13(c) and (d). We observe S-2p peak in 162–164 eV region and shift in  $Cu-2p_{3/2}$ peak from 933.9 eV to 932.9 eV indicating formation of CuS from CuO. Formation of CuS has also been reported in earlier studies [9]. CuS being metallic leads to reduction in resistance on exposure to H<sub>2</sub>S. On the other hand, removal of adsorbed oxygen on interaction with H<sub>2</sub>S results in increase of resistance. Both these processes compete to give complex response on exposure to  $H_2S$ . Better response and recovery times at high temperatures are attributed to increased reaction rates at high temperature. The reduction in response component corresponding to adsorbed oxygen at high temperature is understandable as physisorption of gases is reduced at higher temperatures.

Isolated CuO nanowires aligned between two gold electrodes showed good sensitivity for both  $H_2S$  and NO gases at room temperature. Exposure to  $H_2S$  (see Figure 14(a)) showed decrease in resistance indicating response dominated by formation of CuS with very fast response (~60 s) and recovery times (~30 s). It may be noted that this data has been acquired at room temperature and sensors at higher temperatures may show even better characteristics. Better sensitivity in case of isolated wires is attributed to better mobility of crystalline nanowires while better response and recovery characteristics may arise due to interaction on thin surface layer only (as isolated nanowires are not porous). On exposure to NO gas (Figure 14(b)), increase in resistance was observed with fairly high sensitivity (~200% for 200 ppm gas) as well as small response and recovery times. Mechanism of increase in resistance on exposure to NO instead of decrease expected for p-type semiconductor is not understood and needs further investigations.

Figure 13 Resistance change on exposure of CuO flakes to different concentration of H<sub>2</sub>S gas at (a) room temperature and (b) 200°C. Inset of Figure (a) shows response for 50 ppm H<sub>2</sub>S and NO gases at room temperature. XPS spectra after exposure to 250 ppm of H<sub>2</sub>S gas in (c) S-2p region and (d) Cu-2p<sub>3/2</sub> region. For comparison, the spectra of unexposed sample are also shown in Figure (d)



For comparison gas-sensing properties were also studied for CuO thin films made by oxidation of thermally evaporated copper films. The films were exposed to different concentration of  $H_2S$  gas at room temperature and the results are shown in Figure 15. In this case only increase in resistance was observed for exposure up to 50 ppm gas, in accordance with p-type behaviour of the films. The recovery in this case was found to be very slow. A comparison of three types of CuO sensors indicates that isolated nanowires have best response for detection of  $H_2S$  and NO gases. These also show faster response and recovery characteristics.



Figure 14 Room temperature gas-sensing characteristics of isolated CuO nanowires measured by change in resistance (*R*) on exposure to (a) H<sub>2</sub>S and (b) NO gases

Figure 15 Change in resistance (*R*) of CuO thin films to  $H_2S$  gas at different concentrations at room temperature. Inset shows expanded view of characteristics obtained on exposure to 1 ppm of  $H_2S$  gas



#### 3.3 ZnO nanowires

ZnO and Zn nanostructures could be prepared by heating Zn metal or a mixture of ZnO and graphite under partial pressure of oxygen [31,32]. ZnO nanowires and tetrapods (four wires joined at one point) with different diameters could be prepared by varying the growth conditions. Here, we describe growth of ZnO nanowires by heating a mixture of ZnO and graphite in 3:1 ratio (by weight) at atmospheric pressure. The material was heated to  $1050^{\circ}$ C under a constant flow (500 sccm) of argon with a heating rate of  $6^{\circ}$ C/min. For preparation of different structures as nanowires and tetrapods, oxygen was introduced in the furnace at different temperatures while heating. The furnace was maintained at highest temperature for 5 h and nanostructures deposited in the quartz tube at different temperatures were collected and analysed. In the following we describe nanostructures obtained on introduction of 4–10% oxygen at temperature of

- 700–900°C
- few minutes after attaining temperature of 1050°C.

In first set of experiments, 4% oxygen was introduced 10 min after furnace reached the highest temperature of 1050°C. SEM micrographs of different samples are shown in

Figure 16 and XRD spectra are shown in Figure 17. The nanostructures collected at 200–300°C were found to be Zn polyhedra (Figure 16(a)). This was shown by absence of oxygen in EDX spectra (not shown here) and XRD (Figure 17(a)). At higher temperatures (300–500°C), spherical balls were obtained and some of the balls at temperatures above 400°C were seen to be broken and partially hollow as shown by arrows in Figure 16(c). XRD of these balls (Figure 17(b)) showed both Zn metal and ZnO peaks indicating that Zn metal balls are formed during initial evaporation when heating source to 1050°C and maintaining at this temperature for a 10 min (in absence of oxygen). These are subsequently oxidised. As the melting point of ZnO is 420°C, hollow spheres may be formed by partial evaporation of Zn metal core and outer ZnO layer yields a core-shell like morphology of spheres. At higher temperatures, ZnO nanowires were observed to grow from these Zn/ZnO spheres. Nucleation of nanowires is clearly seen as small protrusions in Figure 16(d) and these lead to the growth of nanowires as has been observed at higher temperatures (Figure 16(e)).

Figure 16 SEM micrographs of samples obtained by introduction of oxygen after attaining temperature of 1050°C: (a) Zn polyhedra in the temperature range of 200–300°C, (b) spherical balls having core shell structure in temperature zone of 300–400°C, (c) hollow spheres as indicated by arrows in the temperature range of 400–500°C, (d) nucleation of nanowires at temperature of ~500°C and (e) growth of nanowires in temperature range of 550–700°C. Figure (f) shows nanowires/nanobelts obtained in temperatures zone of 400–500°C on addition of oxygen at source temperature of 700–900°C (see online version for colours)



In second set of experiments, oxygen (10%) was added during the heating cycle at a temperature in the range of 700–900°C. In this case growth of Zn metal polyhedra was observed at temperatures of ~200–250°C and that of ZnO nanowires/nanobelts at higher temperatures of 400–500°C (Figure 16(f)). XRD (Figure 17(c)) showed the nanowires/nanobelts to be nearly pure ZnO. XPS spectra of nanowires (Figure 18) also showed these to be ZnO. The nanowires are seen to have typical lengths in the range of several  $\mu$ m and diameter of 50–150 nm.

UV-Visible absorption spectrum was recorded for ZnO nanowires dispersed in ethanol and the results are shown in Figure 19. To determine the band gap we have

plotted  $(ahv)^2$  as function of hv and the band gap was found to be 3.18 eV that is in accordance with the band gap of the bulk crystal. There is no obvious change in the band gap of ZnO nanowires because diameter of wires is of the order of 50–150 nm, which is much larger than the Bohr radius of ZnO (~2 nm).

Figure 17 XRD spectra of samples deposited with introduction of oxygen after attaining source temperature of 1050°C: (a) 200–300°C: zinc polyhedra and (b) 300–400°C: Zn/ZnO core/shell spheres. (c) ZnO nanowires/nanobelts grown at 400–500°C with 10% oxygen added at 700–900°C



Figure 18 XPS spectra of ZnO nanowires



Figure 19 Absorbance vs. wavelength and absorption spectra plotted as  $(\alpha h v)^2$  vs. *E* for determination of energy gap for ZnO nanowires



Two types of sensors were prepared with ZnO nanowires:

- films by dispersion of nanowires in organic solvent and deposition on alumina
- isolated nanowire/nanobelt sensors.

The sensors were investigated for their response to several toxic gases ( $H_2S$ ,  $NH_3$ , NO, CO and  $CH_4$ ) at room temperatures. Films exhibited good sensitivity towards  $H_2S$  and NO gases and very little or no response to other gases. Response of a typical film to different concentration of  $H_2S$  and NO gases is shown in Figure 20. It is seen that the films have good response to both gases at room temperature. Typical response and recovery times at 10 ppm concentration are 250 s and 700 s for  $H_2S$  and 250 s and 150 s for NO respectively. The response and recovery times were found to increase with concentration.





Isolated nanowire/nanobelt sensors were found to have good response to NO gas when nanobelts were used (Figure 21) while the response of nanowires was found to be much smaller. This is possibly due to much smaller thickness of nanobelts (<20 nm) compared to diameter of nanowires. The isolated nanobelt samples showed good response to NO gas with very small response and recovery times of 1.5 s and 3 s respectively at 10 ppm concentration. Comparison with data of Figure 20 indicates that the sensitivity of isolated nanobelts is similar to that of films but the response and recovery times are significantly better. This could be due to crystalline nature of nanobelts where interaction occurs at surface only while in case of films, gas needs to diffuse between the grain boundaries. Isolated nanowires/nanobelts were found to have no response to H<sub>2</sub>S gas in contrast to nanowire films. This indicates that response of films to H<sub>2</sub>S arises due to change in the resistance of grain boundaries only. The study indicates that selectivity of response of a sensor may be improved by tailoring the microstructure and that selective NO sensors may be prepared by use of isolated nanobelts.



Figure 21 Response (S) curves of a sensor with isolated ZnO nanobelts on exposure to 10 ppm of NO gas. Inset shows SEM micrograph of an isolated sensor device (see online version for colours)

#### 3.4 Heterostructure nanowires

Hierarchical heterostructures consisting of nanowires grown on larger nanowire stem are of interest due to their potential in the realisation of three dimensional nanodevices as the cores and branches of these nanostructures are of different materials with different band gap and work function. We have prepared hierarchical heterostructures of A:  $W_{18}O_{49}$  (where A is SnO<sub>2</sub>, ZnO and CuO and  $W_{18}O_{49}$  is oxygen deficient phase of WO<sub>3</sub>). Heterojunctions with SnO<sub>2</sub> and ZnO are n-n type while that with CuO are of p-n type.

The growth of A:  $W_{18}O_{49}$  hierarchical heterostructures was carried out in two steps. In the first step, nanowires of SnO<sub>2</sub>, ZnO and CuO were grown as discussed above. In the second step,  $W_{18}O_{49}$  nanowires were grown on these nanowires by thermal evaporation of tungsten using a vacuum system at a pressure of  $2.5 \times 10^{-4}$  mbar maintained by flow of air. For this purpose, nanowires were placed at a distance of ~2 cm from tungsten filament and depositions were carried out for 30 min at a source temperature of ~1965°C measured using a pyrometer. The deposition occurs by oxidation of tungsten filament followed by evaporation as oxides of tungsten are volatile with a vapour pressure of  $10^{-4}$  mbar at 980°C for WO<sub>3</sub>. The substrates (CuO, ZnO. SnO<sub>2</sub> nanowires) were not intentionally heated but during deposition their temperature increased to 700°C. A uniform blue deposit of  $W_{18}O_{49}$  nanowires was obtained on base nanowires.

SEM micrographs of typical heterostructures are shown in Figure 22. We observe needle like growth of  $W_{18}O_{49}$  on the surface of template nanowires with diameter of 50–70 nm and length up to 1  $\mu$ m. The length and diameter of these needles was found to vary with oxygen partial pressure. Similar results with higher density and length of  $W_{18}O_{49}$  nanowires were obtained in case of growth with pure oxygen instead of air as shown in Figure 23.

The XRD spectra of typical heterostructures of  $SnO_2$ : $W_{18}O_{49}$  are given in Figure 24 along with that for pure  $SnO_2$  nanowires and thin films of tungsten oxide deposited on alumina substrate (by the same process as deposition of tungsten oxide nanowire on  $SnO_2$  nanowires). We observe two different sets of peaks in the heterostructures, one pertaining to  $SnO_2$  and other to  $W_{18}O_{49}$ . The peaks were indexed to pure  $SnO_2$  rutile phase with a = 4.74 and c = 3.1885 Å and monoclinic  $W_{18}O_{49}$  phase (oxygen deficient

WO<sub>3</sub>) with a = 18.33, b = 3.786, c = 14.04 Å. No impurity or mixed phases were detected indicating that the heterostructures are composed of pure SnO<sub>2</sub> and W<sub>18</sub>O<sub>49</sub>.

The heterostructures were further probed by determination of band gap using optical absorption spectroscopy and the results for  $ZnO:W_{18}O_{49}$  are shown in Figure 25. Two band gaps of 3.17 eV and 2.85 eV corresponding to ZnO and WO<sub>3</sub> were recorded. The results indicate that there is no interaction between the two metal oxide semiconductors.

Gas-sensing characteristics of sensors fabricated using single wires as well as films of SnO<sub>2</sub>:W<sub>18</sub>O<sub>49</sub> heterostructures were studied. Both types of sensors showed change in resistance on exposure to H<sub>2</sub>S and Cl<sub>2</sub> gases while no response was observed for NO, CO,  $CH_4$  and  $NH_3$  gases. For film type sensors (Figure 26), exposure to  $Cl_2$  shows a resistance change by factor of 5 while for H<sub>2</sub>S it is by a factor of 3. For Cl<sub>2</sub> gas the response and recovery times are  $\sim 8$  min and 30 min respectively. Corresponding values for H<sub>2</sub>S are 30 s and  $\sim$ 120 min respectively. Single nanowire sensors showed a change in resistance by a factor of 14 and 2 for  $Cl_2$  and  $H_2S$  respectively. These sensors therefore show significant selectivity for detection of chlorine. An interesting observation is that on exposure to chlorine gas, the resistance of the single wire sensors is found to decrease (opposite to that expected for an oxidising gas) in contrast to film type sensor (that have expected increase in resistance). The opposite response of film and single wire sensors to chlorine is attributed to difference in the interaction of chlorine gas with the adsorbed and lattice oxygen atoms as discussed above for pure  $SnO_2$  nanowires [27]. Differences in response to chlorine gas for these two different sensors shows that a combination of single nanowire heterostructure and film type sensor may be used for highly selective detection of H<sub>2</sub>S and Cl<sub>2</sub> gases.

Figure 22 SEM micrographs of (a)  $SnO_2$ :  $W_{18}O_{49}$ , (b) ZnO:  $W_{18}O_{49}$  and (c) CuO:  $W_{18}O_{49}$  nanowire heterostructure grown in presence of air at a pressure of  $2.5 \times 10^{-4}$  mbar



Figure 23 SEM images of (a)  $SnO_2$ :  $W_{18}O_{49}$  and (b) CuO:  $W_{18}O_{49}$  nanowires grown in presence







Figure 24 XRD spectra of (a)  $SnO_2$  nanowires, (b)  $W_{18}O_{49}$  thin films and (c) heterostructures of  $SnO_2$ : $W_{18}O_{49}$ 

Figure 25 Optical absorption spectra of ZnO:W<sub>18</sub>O<sub>49</sub> heterostructures



Figure 26 Response (S) of sensors prepared using  $SnO_2$ : $W_{18}O_{49}$  heterostructures to  $H_2S$  and chlorine gases at room temperature; (a) film type sensor and (b) single nanowire sensor



# 4 Conclusion

One-dimensional nanostructures of  $SnO_2$ , CuO, ZnO and their hierarchical nano-heterostructures with  $W_{18}O_{49}$  have been prepared. The nanostructured materials were found to show good response for detection of gases at room temperature. It is seen

that copper may be doped in nanowires of  $SnO_2$  in contrast to that in bulk material providing additional possibilities to improve characteristics of sensors. In general response of intragrain and grain boundary regions is also found to be different and this helps in tailoring the gas sensor characteristics via control of microstructure. Response and recovery times of sensors prepared using isolated 1D structures are found to be much smaller in comparison to nanowire films indicating their potential. Initial results on application of hierarchical heterostructures for gas sensing have been reported. Such structures have not been much investigated earlier and there is a need to carry out studies in this direction to take advantage of sensing characteristics of heterojunctions in oxide semiconductors.

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