Quasi one dimensional metal oxide nanostructures for chemical sensing application

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NANYANG
TECHNOLOGICAL
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**QUASI ONE DIMENSIONAL METAL OXIDE
NANOSTRUCTURES FOR CHEMICAL SENSING APPLICATION**

NANDAN SINGH

School of Materials Science & Engineering

2012

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NANOSTRUCTURES FOR CHEMICAL SENSING APPLICATION**

NANDAN SINGH

**A thesis submitted to the Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy in
Engineering**

2012

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UNIVERSITY**

**School of Materials Science & Engineering
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Summary

Quasi one dimensional (1D) nanostructures are potential candidates to meet the challenges for the realization of future sensors. They offer many advantages over thin film based sensors such as higher crystallinity, high surface-to-volume ratio, low power consumption, long channel with small cross sectional area which controls the conductance.

In this thesis, the properties of metal oxides (MOx) nanowires in a field effect transistors (FET) configuration are studied. Mainly the electronic and chemical sensing properties of In_2O_3 based nanowires have been established. Quasi 1D nanostructures are synthesized in horizontal tube CVD furnace based on VLS mechanism. Different morphologies are obtained by varying the growth conditions such as; growth temperature, pressure and growth duration. In_2O_3 nanowires (with diameters of 25-90 nm and length of 10-50 μm), nanotowers (with diameter 100-150 nm and length below 10 μm) and long layered nanorods (with a diameter of 200-400 nm and length of 20-50 μm) are grown through carbothermal reduction of In_2O_3 powder by varying source temperature in a CVD horizontal furnace. VLS-VS competitive growth is proposed for the formation of layered nanorods at higher source temperature. As deposited nanowire samples on alumina substrates are used as a gas sensor. Pristine In_2O_3 , Zn-doped In_2O_3 and In_2O_3 -ZnO core shell nanowires are used to test various pollutant gases under the resistor configuration. Such devices have shown optimum sensor response at higher working temperature. It is observed that pristine In_2O_3 nanowires have shown better sensor response towards NO_2 gas while Zn-doped In_2O_3 and

In₂O₃-ZnO core shell nanowires have shown superior sensor response for ethanol, H₂, CO and acetone (reducing gases).

Nanowire FET (NW-FET) devices are fabricated on highly doped Si substrate using SiN_x as gate dielectric layer and bottom gate configuration. Photolithography process is used to design the microelectrodes for NW-FET device. Further, gas sensing mechanism on single and network nanowire sensors is investigated by comparing doped and undoped, Ohmic and Schottky contact devices. A highly sensitive device for CO gas sensing at room temperature is fabricated using gold nanoparticle functionalization. High coverage of gold nanoparticles on nanowire channel is obtained using a self assembled monolayer of *p*-amino-phenyl-trimethoxy-silane. The sensor response for CO gas is observed to be depending on gold nanoparticle coverage.

It is observed that devices with Schottky contacts, Zn doping and core-shell hetero-structures have shown improved sensor response for reducing gases (e.g. CO, H₂, ethanol, acetone etc.) in contrast to the pristine nanowires and devices with Ohmic contact. Schottky contact devices have shown a better sensor response for reducing gases and Ohmic contact devices have shown a better sensor response for oxidizing gases. Similarly In₂O₃-ZnO core shell hetero-structures have shown better response for reducing gases (e.g. CO, H₂, and ethanol). Highly sensitive NW-FET devices are fabricated by understanding the role of contact resistance. We have developed highly sensitive devices operating at room temperature by utilizing the contact resistance and coupling it with the nanowire channel functionalization with Au nanoparticles. This work provides a promising approach to fabricate room temperature working devices with excellent sensing capabilities.

Chapter 1

Introduction

1.1 Background and Motivation

Recent advancements in the synthesis and characterization of quasi one-dimensional (1D) nanoscale materials are driven by the need to understand their novel electronic properties for the potential applications in the fabrication of nano-devices. Among the various nanostructures, nanowires have received much research attention for more than one decade. These nanowires have created opportunities for fundamental physics and high-performance devices where nanowires are used to design small and ultra fast electronic and optical devices. In the field of chemical sensing, nanowires offer several advantages such as; high surface-to-volume ratio, monocrystalline assembly and easy growth techniques. These advantages can be implemented to develop a smart sensing device which can operate at low temperature.

Metal oxides (MOx) represent an attractive class of materials. The electronic properties of MOx cover the range from metals (conductors) to semiconductors and insulators. MOx at their perfect stoichiometric ratio behave as insulator. When controlled oxygen vacancies are created, MOx behave as semiconductors. Highly conductive MOx (comparable to metal) can be achieved via doping (e.g. Sn-doped In_2O_3). The interest in MOx continues for last few decades, as seen from an increase in the relevant number of

publications. The interest in In_2O_3 is fueled by its prospects in applications due to its direct wide band gap ($E_g \sim 3.65$ eV at room temperature), optical transparency, high electrical conductivity and its environment friendly and stable nature. The strong photoluminescence (PL) of In_2O_3 in the visible and ultraviolet (UV) region makes it a potential candidate for optical use. For application as a transparent conducting oxide (TCO) material, a high conductivity with optical transparency is desired. In a stoichiometric MOx, it is very difficult to obtain the simultaneous optical transparency with high electrical conductivity.¹ One of the ways to produce it is by controlled doping or by creating non-stoichiometry during material growth.

The growth and synthesis of metal oxide semiconductor nanowires (e.g. In_2O_3 , SnO_2 , ZnO etc.) have been well established and studied for past one decade. Different growth techniques have been applied to produce 1-D nanostructures. In majority of the methods, nanowires have been grown using a seed (catalyst) which mainly controls the morphology and dimensions of the nanostructure. The devices have been fabricated by transferring the 1-D nanostructures on a different substrate or using the as grown sample as platform. The potential application areas of metal oxides include; optoelectronics, chemical and bio-molecular sensing, transparent conducting devices, high speed nanowire transistors for logic gates and memory devices, high energy density capacitors, solar cells, etc.

In the nanoscale regime, materials exhibit distinctively different electronic and physical properties from their bulk counterpart. Nanowires offer high surface-to volume ratio which makes them a potential candidate for chemical sensing. Thus the enhanced sensitivity in comparison to thin/thick films, allows developing chemical sensing devices which can be operated at room temperature. In_2O_3 is a potential material for sensing of NO_2 , CO , H_2S , H_2 ,

ethanol, and ozone. In the last few decades, a lot of chemical sensing research work has been performed on thin film/network nanowire based resistor devices. These devices need high temperature to perform any sensing operation. The use of high temperature reduces the device life time and consumes large power. In the recent years, more efforts are focused on the possible room temperature operation. Single nanowire based sensor devices have shown possible room temperature operation. The main device is the nanowire field-effect-transistor (NW-FET), where an electric field is applied via gate electrode to enhance the reaction kinetics during sensing. Room temperature operation allows the sensor device to explore sensing on explosive and hazardous chemical species which is unsafe at high temperature. Other advantages of room temperature operation are; low power consumption, longer life time and better stability. The selectivity for a particular gas can be achieved either via controlled doping with suitable dopant or surface modification of the nanowire using suitable metal to enhance catalytic reactions. Single NW-FET configuration is more suitable to study the fundamental sensing mechanism of chemical and biological sensors. The influence of sensing material (which is used as nanowire channel) and the nanowire contacts can be explored using such device configuration. Accordingly, the optimization of the influencing parameters can achieve high sensitivity and selectivity.

1.2 Objectives

The main objectives of the present work are categorized as follows:

- ❖ Controlled growth and characterization of wide band gap metal-oxide semiconducting nanowires based on In_2O_3 .
- ❖ To develop the room temperature chemical sensing capabilities of single nanowire based devices and study the chemical sensing mechanism of the single nanowire devices, with modification of the nanowire to enhance the sensitivity at room temperature operation.
- ❖ To study the effect of doping and hetero-structured nanowires on the room temperature chemical sensing properties of various pollutant gases.

1.3 Scope

This thesis investigates the synthesis of semiconducting MO_x nanowires and their device applications in chemical sensing. Much emphasis has been put towards the exploration of room temperature operation of the sensor devices. Single nanowire based sensor devices were used in most of the experiments to explore room temperature operation. The influences of nanowire channel and metal-semiconductor contacts at two ends of the nanowires on gas sensing have been studied at room temperature. Highly sensitive CO gas sensors were fabricated by functionalizing gold nanoparticles on nanowire surface via enhanced catalytic CO gas oxidation. All nanowires (doped, undoped and hetero-structures) were produced in a CVD furnace by VLS (vapor–liquid–solid) growth mechanism. Characterizations of the grown nanostructures were carried out by X-ray Diffraction (XRD), Field-Emission Scanning

Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDS), Transmission Electron Microscopy (TEM), Kelvin probe force microscopy (KPFM), Photoluminescence (PL), and Raman Microscopy. I-V and sensing measurements on the Nanowire Field Effect Transistor (NW-FET) devices were carried out using the electrical probe-station.

1.4 Organization of the thesis

Chapter 2 introduces the literature review on the pioneer and latest work done in the area of chemical sensing based on the semiconducting quasi 1D nanostructure devices. Other areas such as; different growth techniques, optical and electrical properties before and after doping nanowires, effect of doping on chemical sensing are reviewed as well.

Chapter 3 summarizes the experimental part of the project. Mainly the nanowire synthesis method has been discussed in detail. Modified VLS furnace is described in detail. Introduction to gas sensing and device fabrication methodologies have been included. Nanowire alignment using dielectrophoresis method is described in detail and optimization of the parameters for single nanowire alignment is discussed. Other minor individual experimental details are included in the corresponding chapters/sections.

Chapter 4 covers the quasi 1D MO_x nanostructures growth. Synthesis and morphological characterization of pristine and Zn-doped In₂O₃ 1D nanostructures were presented. Effects on the morphology of nanostructures due to the variation in experimental parameters are discussed. Optical characterizations of these nanostructures are also presented.

Chapter 5 deals with sensing characterizations of resistor based devices. Pristine In_2O_3 , Zn-doped In_2O_3 , In_2O_3 -ZnO core-shell hetero-structures are tested for CO, NO_2 , H_2 , ethanol and acetone at a working temperature of 100-500°C under a relative humidity (RH) of 50%. Effect of RH variation on the sensor response is also discussed.

Chapter 6 mainly consists of the work done on the single nanowire FET based sensors at room temperature. This chapter is divided into two main sections. First section describes the effect of contacts between semiconductor-nanowire and metal-electrode on the sensing of oxidizing and reducing gases. The details regarding CO and NO gas sensing on Schottky and Ohmic contact devices are presented. Second section describes the effect of channel doping on sensor response. Zn-doped In_2O_3 nanowires are used to study the effect on the sensing of CO gas at room temperature.

Chapter 7 introduces the effect of nanowire channel surface modification on the sensing response of CO gas at room temperature. Highly sensitive devices were fabricated for the CO gas sensing at room temperature, utilizing high surface coverage of AuNPs on a Schottky contacted device. The effect of different Au loading time on the CO sensing is also demonstrated.

Chapter 8 will conclude the report and lists the future directions.

1.5 Major contributions of the thesis

The major contributions achieved in this research work are summarized as follows;

1. High yield of nanowires was achieved using a modified VLS process. The layered nanorods and nanotowers have been synthesized by controlling the growth temperatures.
2. The effect of Zn- doping and hetero-structures (In_2O_3 -ZnO core-shell nanowire) on reducing and oxidizing gases, in a nanowire network resistor have been investigated. Reducing gases have shown enhanced sensor responses for both Zn- doped and hetero-structured nanowire compared to pristine In_2O_3 nanowires, which helps in the selection of the devices for different classes of gases for higher sensitivity.
3. Sensing behavior of different classes of gases on single nanowire FET based Ohmic and Schottky contact devices at room temperature is explored. Schottky devices (higher contact resistance) are identified to be better sensors for reducing gases and Ohmic devices are superior for oxidizing gases.
4. CO gas sensing down to 200 ppb at room temperature is successfully achieved by catalytically enhanced CO oxidation on NW-FET. The high sensitivity was achieved by utilizing high coverage of Au nanoparticles functionalization on In_2O_3 nanowire Schottky contact device. A self assembled monolayer of *p*-amino-phenyl-trimethoxy-silane was introduced to increase the AuNPs attachment on the nanowire surface for the first time.
5. The possible room temperature gas sensing has been shown by using a single nanowire FET device. Highly sensitive and selective NW-FET devices for CO gas at room temperature are demonstrated.

Chapter 2

Literature Review

In this chapter, an introduction of the working principle on the conductometric solid state chemical sensor is presented. The advantages of the emerging research on the quasi 1D-nanostructures based solid state gas sensors are discussed. The recent progresses and pioneered work done in the field of chemical sensing are presented. Detailed structural, electrical, optical and sensing properties of In_2O_3 nanowires are illustrated.

2.1 Solid state chemical sensors

Chemical sensors have gained much attention in recent time for applications that include environmental monitoring, home-land security, military and food safety. Solid state chemical sensor is a general term represents a variety of sensors constructed of semiconductor, metal, insulator and organic membrane. The widely known solid state chemical sensors include semiconducting metal oxide based sensors, silicon based sensors, catalytic sensors, solid electrolyte sensors, and membranes based sensors.

Amongst a variety of nanomaterial, MO_x based quasi 1D-nanostructures (e.g. nanowires, nanotubes, etc.) have shown promising potential for future sensors. Nanowires based sensors have been mainly characterized as: impedometric, conductometric (resistor based) and field effect transistor (FET) based chemical sensors.

Impedometric sensors, as the name suggests are based on impedance change upon exposure to chemical species. These sensors are operated under alternating voltage. There are thin film and nanowire based impedometric sensors² but this class of chemical sensors have not received as much researcher's attention as the conductometric based chemical sensors have received.

Working principle of a conductometric chemical detector is based on the relative change in conductance of the sensor surface upon exposure to a particular chemical.³ The conductometric gas sensors have been fabricated mainly from thin film or nanostructure network.³ In such devices, thin film or nanowire network is contacted at the two ends by two metal electrodes on an insulating substrate with a typical separation of more than 50 μm . Insulating substrates such as alumina have been mainly used to minimize the leakage through substrate in such devices.

In the NW-FET based sensors, single/network nanowire has been used as an active channel to interact with the gas molecules. Bottom gate contact configuration has been preferred due to the simplicity in device fabrication on highly doped Si substrates. A gate dielectric is used to isolate the gate electrode to nanowire channel. The working principle of NW-FET based sensors is that the chemical species adsorbed onto the nanowire channel surface which works as an extra gate.⁴⁻⁶ The effect of sweeping gate bias voltage gives the advantage over two terminal based (resistor) sensor devices.⁶ The field is applied through the gate electrode to tune the conductance of the nanowire channel and improve the surface reaction kinetics during gas exposure.

Sensing mechanism of conductometric and FET chemical sensors is based on the change of conductance of the nanowire channel upon exposure to chemical species.^{4, 7, 8}

Upon exposure of gases to nanowire, gas molecules adsorb on the nanowire surface and change the initial conductance of the device. There are mainly two types of adsorptions, viz., physisorption, and chemisorption.⁹ In physisorption, there is no electronic exchange involve between chemical species and active material. In chemisorption, electronic exchange between the adsorbed gas molecules and the nanowire are involved. The chemisorbed species (e.g. chemisorbed oxygen and water species) at the surface intermediates the charge transfer processes between gas molecules and MOx nanowire.⁹ The effect of oxygen related defects of a single ZnO nanowire on gas-sensing properties have been investigated by *Ahn et al.*¹⁰ It was found that the NO₂ gas sensitivity was linearly proportional to the oxygen-vacancies present in the nanowire. This work shows the role of oxygen vacancies in chemical detection using MOx. Figure 2.1 shows the schematic illustration of single nanowire conductometric device.

Figure 2.1 Schematic illustration of the conductometric nanosensor.

At elevated working temperatures, semiconducting oxides have shown changes in electrical properties according to the composition of the chemical species to which they are exposed.¹¹ In ambient conditions, metal oxides are high melting point materials, but many of them either sublime or decompose at low pressure, making thermal evaporation a possibility. The choice of possible oxide is mainly constrained by the temperature at which a particular oxide evaporates easily and the ease of fabrication.

Semiconducting metal oxides, mainly In_2O_3 , ZnO and SnO_2 have attracted the attention in gas and bio- sensing under atmospheric conditions. In_2O_3 is an important material with wide ranging applications in the areas such as; chemical/bio-molecule sensing, transparent oxide based TFTs, optoelectronic devices, etc.¹²⁻¹⁵ Therefore high quality In_2O_3 nanostructures synthesis is important for exploring the electronic properties for the application in nanoscale devices.^{16, 17}

The increasing interest in In_2O_3 nanostructures lately can be seen from the surge in the relevant number of publications in recent years. The interest in In_2O_3 is fueled by the applications utilizing its direct wide band gap ($E_g \sim 3.6\text{-}3.75$ eV at room temperature), optical transparency, electrical conductivity and its environment friendly and stable nature. However, there has been some debate lately, regarding the band gap of In_2O_3 . Recently some reports have shown a smaller direct band gap $E_g \leq 3$ eV¹⁸⁻²⁰ instead of the old which thought to be ~ 3.75 eV.^{21, 22} The surface electronic properties of In_2O_3 have also been debated on the electrons depletion layer at the surface which was long been thought to be at the surface,^{23, 24} instead an accumulation of electrons at (001) surface has been investigated in high quality single crystalline material.^{19, 25}

Sn-doped In_2O_3 (ITO) is the widely used transparent conducting oxide (TCO) material. The combination of high electrical conductivity with high optical transparency in the visible region makes ITO an important material for the wide range of applications in optoelectronic devices.^{13, 15} However, in an intrinsic stoichiometric MOx semiconductor, the simultaneous optical transparency with high electrical conductivity is not possible. There are two ways to obtain it in MOx, e.g. doping and creating oxygen vacancies or excess metal ion interstitials during growth.^{26, 27}

2.1.1 Crystal structure of Indium Oxide (In_2O_3)

In_2O_3 , exists in two phases of cubic bixbyite and hexagonal corundum-type.²⁸ The *cubic*- In_2O_3 phase is easily formed. The corundum-type *h*- In_2O_3 structure has been rarely prepared due to the requirements of extremely high temperatures and pressures.²⁹⁻³² The crystal structure of In_2O_3 in its cubic form is bcc (body centered cubic) with space group Ia-3 and lattice constant $a = 10.118 \text{ \AA}$.³³ According to Wyckoff notation, out of the 80 atoms in the *c*- In_2O_3 unit cell, *b*-sites occupy 8 In atoms, *d*-sites occupy 24 In atoms and *e*-sites occupy 48 oxygen atoms. In atom in each *b*-site is surrounded by six O atoms at the same inter atomic distance of $2.19 \text{ \AA}$. On the other hand, In atom in *d*-site is also surrounded by six O atoms with three different inter atomic distances of 2.12, 2.19, and $2.21 \text{ \AA}$.³³ *a*- and *c*-sites remains unoccupied.

Figure 2.2 Schematic of the bravais unit cell of the *c*-In₂O₃.

The metastable phase corundum-type (hexagonal structure) In₂O₃, is a route toward creating new materials,³⁴ but limited studies on the preparation and properties of corundum-type In₂O₃, especially its nanostructures, have been reported. Gurlo *et al.*³⁵ prepared corundum-type In₂O₃ particles and Qian's³⁶ group prepared corundum-type In₂O₃ nanofibers by annealing the InOOH precursor.

2.2 Nanostructures

With the advancement of characterization, it has become easier to characterize material in the nanoscale level. As a result, large numbers of nanostructures have been synthesized by researchers with different dimensions. Quasi one dimensional (1D) nanostructures mainly

include; nanowire, nanorod, nanotube, nanobelt, nanotower, nanoarrow, etc. Hierarchical nanostructures, such as nanocomb, nanobrush, nanotree nanoflower, etc. with higher dimensions have been synthesized where the secondary arms grown on the main 1D core.

Figure 2.3 A schematic illustration of different types of quasi-1D MO_x nanostructures, starting from the left to right; Nanowires, core-shell nanowire, nanotubules, heterostructures, nanobelts, nanotapes, dendrites, hierarchical nanostructures, nanosphere assembly and nanosprings [adopted from 37].

1D nanostructured systems have attracted much attention in recent years in areas such as optoelectronics, chemical sensing, etc. The synthesis of 1D nanostructure has found intensive research attention because of the contributions to the understanding of basic concepts and potential technological applications. 1D nanostructures are the smallest dimension for charge carriers transport between two electrodes, which makes them an ideal building blocks for the application in electronic nanodevices.

The synthesis of In₂O₃ nanostructures are less reported compared to those for ZnO or SnO₂ nanowires. It may be due to the growth of the In₂O₃ nanostructures is difficult by a simple physical method. Intrinsic high symmetry of the cubic In₂O₃ may be the reason for difficult growth. Metal catalysts, such as Au or Ag are often tried to overcome this problem.

Metal catalyst allows a highly oriented growth of nanostructure through vapor-liquid-solid (VLS) mechanism.³⁸⁻⁴¹ The final products depend strongly on the growth conditions including growth temperature, vapor pressure of the precursors and oxygen concentration.

By adjusting growth parameters, novel structures of the In_2O_3 can be obtained. Nanowires, novel nanoarrows and nanorods of In_2O_3 have been synthesized by *Y. Yan et al.*⁴² using a catalyst in the chemical vapor deposition (CVD) route. They have proposed a growth mechanism based on the morphology of the different nanostructures. A competitive growth mechanism between the solid-liquid interface and epitaxial growth on nanowire's surface have suggested for rectangular cross sectional nanowires.

2.3 Deposition techniques

The as grown nanostructures properties (such as morphology, crystallinity, electrical and optical properties) are affected by their synthesis technique. Over the years, various methods are used to produce quasi 1D nanostructured materials. Some techniques have been explored extensively, while others have attracted less attention. Main techniques can be generally grouped according to the synthesis process, as follows:

(1) Spontaneous growth:

- (a) Evaporation (or dissolution)-condensation
- (b) Vapor (or solution)-liquid-solid (VLS or SLS) growth
- (c) Stress-induced recrystallization

(2) Template-assisted synthesis:

- (a) Electroplating and electrophoretic deposition
- (b) Colloid dispersion, melt, or solution filling

(c) Conversion with chemical reaction

(3) Electrospinning

(4) Lithography

First three techniques are considered as bottom-up techniques, whereas the fourth technique is a top-down technique. Spontaneous growth has been explored extensively and commonly results in the formation of single crystal nanowires or nanorods along a preferential crystal growth direction. Template assisted synthesis mostly produces polycrystalline or even amorphous products. In this work, we are using VLS growth to grow In_2O_3 nanowires using gold as catalyst and we discussed it in detail in the following section.

Vapor-liquid-solid (VLS) growth mechanism: This mechanism was first proposed in 1964 by Wagner and Ellis for gold-assisted growth of silicon whiskers, is the potential technique to grow 1-D nanostructures.⁴³ VLS was named after V-vapor (precursor), L-liquid (metal catalyst droplet) and S-solid (final product) (Figure 2.4).

Figure 2.4 Schematic representation of VLS growth of nanowires. [Adopted from ⁹].

In the VLS mechanism, catalyst (metal nanoparticle) absorbs the vapor reactants. The catalyst metal particle forms liquid droplet at higher temperature. The catalyst activates the

growth on its surface due to its higher sticking coefficient and vanishing/minimizing elsewhere. The schematic representation of VLS growth is shown in Figure 2.5. The nanowire growth begins at the interface between substrate and catalyst droplet when the catalyst droplet is supersaturated with the precursors. The nanowire growth direction and diameter is mainly controlled by the catalyst droplet.^{43, 44}

Figure 2.5 Schematic representation of the VLS growth mechanism; in step 1, the nucleation on the catalyst droplet, step 2 is growth of the nanowire and final step is termination of the process.

To choose a catalyst for a specific source material to grow under VLS mechanism, there are some requirements to be considered;

- (1) At the deposition temperature, the catalyst must form a liquid solution with the grown material
- (2) The melting point of the catalyst should be low under growth conditions
- (3) The distribution coefficient of the catalyst into the grown material should be less than unity,
- (4) The catalyst must be chemically inert, in order to minimize any by-products

There are ample reports on the VLS grown In_2O_3 nanowires using Ag and Au as catalyst. Ag-induced synthesis of semiconducting In_2O_3 nanostructures has been shown by *Zhang et al.*⁴⁵ In_2O_3 nanowires with diameter 10-100 nm have been synthesized through direct hydrogen reduction In_2O_3 powder and Ag nanoparticles as catalyst. Au catalyzed VLS growth of In_2O_3 nanowires have been reported mainly by carbothermal reduction of In_2O_3 powder. *G. Jo et al.*⁴⁶ have reported high-quality In_2O_3 nanostructures by utilizing Au as catalyst in VLS growth.

VLS growth is the dominant technique for 1D growth of nanostructures. Apart from VLS growth there are reports on VS, and SLS based growth. *Magdas et al.*⁴⁷ has reported a 3-D nanowire networks and complex In_2O_3 nanostructures by thermal treatment of InN powder at temperatures between 350 and 700°C without using any catalyst.

2.4 Characterization of nanostructures

With the advancement in characterization tools, there are various methods can be employed to characterize the as grown nanostructure. The mainly used methods include microscopy, spectroscopy, diffractometry and electrical measurements on single nanowire. In microscopy the commonly used methods are field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and scanning probe microscopy (SPM). In SEM and TEM, the sample is scanned by a highly collimated beam of electrons and different signals from the sample can be monitored to obtain different information. In SPM, sample is scanned by an atomically sharp tip and different forces between sample and tip are monitored in order to obtain the information from the surface of the sample.

In spectroscopic characterizations, electromagnetic (EM) radiations interact with the matter. The interaction mainly controlled by the wavelength of the radiation used. The main interactions include; electronic transition, molecular vibration or electron loss. Some commonly used spectroscopic techniques are Raman spectroscopy, infra red (IR), Fourier transform infrared spectroscopy (FTIR), ultra-violet visible (UV-Vis), EDS and XPS.

Diffraction involves the interaction of X-rays, electrons or neutrons with the atoms in the matter and gives the information mainly regarding the arrangement of atoms in the matter. The most widely used technique is X-ray diffraction (XRD). Electron and neutron diffraction techniques are among the less widely used techniques. Electrical characterizations are the essential measurements to investigate and analyze the sensing mechanism of nanostructures. Therefore, it is thoroughly reviewed to collect more information on the electrical and electronic properties of doped and undoped In_2O_3 based devices.

2.5 Doping

In a conductometric chemical sensor, initial conductivity of the device plays crucial role in sensing of low concentration of reactive gases in air.⁴⁸ An effect is not expected for traces of reactive gases if the conductivity of the device is too high, and if the conductivity is very low (high resistivity), then an effect will be difficult to measure. Hence doping plays an important role to control the conductivity.

Controlled doping into a nanowire is essential to enhance NW-FET performance but still remains a challenging issue. With an electron carrier concentration (10^{16} - 10^{19} cm^{-3}) undoped In_2O_3 is known to be an *n*-type wide band gap semiconductor. The intrinsic *n*-type nature is due to native defects such as interstitial indium, oxygen vacancy etc., which act as

donors in order to generate free electrons.⁴⁹ The conductivity can be further increased in In_2O_3 nanostructures by doping with donors. Sn^{4+} is one of the important donors for In_2O_3 .²⁶ A donor level near the conduction band introduces by substitution of In^{3+} by a tetravalent ion (e.g. Sn^{4+}) or O^{2-} by single valent ion (e.g. F^-). On the other side, an acceptor energy level created near the valence band when the substituting atom is lower valency cations such as Zn^{2+} or Cu^{2+} in In^{3+} sites. In this process, p- type conductivity increases. Increasing n-type conductivity have been mainly focused in majority of investigations,^{26, 27} but there are not many reports on the doping with acceptors for In_2O_3 . Recently *Zhang et al.*⁵⁰ have reported single Zn-doped In_2O_3 nanowire as the driving transistor for organic light-emitting diode. FETs fabricated from Zn-doped In_2O_3 NWs have shown superior device performance which include high mobility ($80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), “high-on-state” current of up to 10^{-5} A and large on/off current ratio of 10^7 . However, the solid solubility of the Zn in In_2O_3 system was found to be very low (0.8 at %).⁵⁰ The solubility limit is reported to be lower than 2.2% at 1250°C in thin films.⁵¹ In contrast, Sn^{4+} doped In_2O_3 nanostructures the solid solubility has been reported up to 21.1 at. %, ²⁶ which is very high in comparison to Zn- In_2O_3 system and a 10^7 times enhancement in the conductivity is also reported.

In contrast of the bulk semiconductors, where the technology is well established for obtaining high quality, doping is still challenging for nanoscale semiconductors. Further improvements in the area of nanowire growth with desired composition and controlled doping is needed to tune the electronic and optical properties of future nanowire based devices.

2.6 Electrical properties of In₂O₃ nanostructures

It is well proven that the ITO possesses interesting electronic and optical properties. ITO is mainly applied as a transparent conducting oxide (TCO) material. ITO thin films are preferred due to the low electrical resistivity and optical transparency in the visible spectra.¹² In₂O₃, in its perfect stoichiometric condition, exhibits high resistivity ($\rho \sim 10^8 \Omega \text{ cm}$) with low free carrier concentration. However, non-stoichiometric In₂O₃ thin films and nanostructures have been grown with high free electron concentration ranges between 10^{18} cm^{-3} and 10^{20} cm^{-3} .²⁶ Oxygen vacancies exist in the In₂O₃ crystal structure so that the formula of the material is In₂O_{3-x}, where x represents the deviation from stoichiometry.²⁶ A linear resistance of 70 M Ω and electron mobility of 71 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for a 5 μm channel length and 5 nm radius undoped In₂O₃ nanowire has been reported by *Zhou* group.⁵² Divalent dopants (e.g. Zn²⁺) into In₂O₃ has been found to enhance the transistor characteristics (such as on-off current ratio, mobility etc.). An increased “on-off current ratio” 10^2 to 10^7 , high mobility ($\sim 80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), “high-on-state” current of up to 10^{-5} A has been reported in Zn doped In₂O₃ system (Figure. 2.6).⁵⁰ The enhanced transistor characteristics are attributed mainly to the Zn insertion in to the In₂O₃ crystal system.

Figure 2.6 I-V plots of Zn-doped In_2O_3 NW-FET; (a) I_d - V_d characteristic of NW-FET at different gate voltage. The inset shows a SEM image of a single NW-FET and (b) I_d - V_g characterization plot at $V_d=1$ V. Drain current is shown in both the linear plots (black line) and logarithmic (red line).⁵⁰

On the other side, Sn-doping in to In_2O_3 have been found to enhance conductance of the device but deteriorates the other transistor characteristics such as carrier mobility and on-off ratio.²⁶ Dandan *et al.*²⁶ have reported ITO nanowires with Sn content of 17.5 at.% with an enhancement in the conductance of over 10^7 times, on-off ratio of 10^3 and poor electron mobility of $0.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The oxygen vacancies concentration in the grown nanostructures tunes the optoelectronic characteristics of the MOx nanostructures.^{53, 54, 6} By controlling the oxygen concentration while synthesizing nanostructures, the optoelectronic properties can be tuned. Zhou group⁵⁴ has reported the tuning of electronic properties in In_2O_3 nanostructures by controlling oxygen concentration. They have synthesized In_2O_3 NWs consisting two types of oxygen vacancies concentrations (0.017% vs. 0.04%), accordingly they have obtained either lightly or heavily doped nanowires ($2.56 \times 10^7 \text{ cm}^{-1}$ vs. $7.16 \times 10^7 \text{ cm}^{-1}$). For heavily doped nanowires, a positive shift in the threshold voltage (annealing in

ambient conditions) and for lightly doped nanowires, a negative shift is also reported. Recently, high performance In₂O₃ nanowires (20 nm diameter) transistors (NWTs) by using self-assembled nanodielectric (SAND) as the gate dielectric has been reported.⁵⁵ They have reported a high on-current of ~25 μ A for a single In₂O₃ NW at 2.0V_{ds}, 2.1V_{gs}, a field-effect mobility of ~1450 cm² V⁻¹ s⁻¹ and an on-off current ratio of 10⁶ with a sub threshold slope of 0.2 V/decade. The mobility was calculated from the extracted g_m and gate-channel capacitance $C_i = 2\pi\epsilon_o k_{\text{eff}} L / \cosh^{-1}(1 + t_{\text{ox}} r)$, using $\mu = \frac{dI_d}{dV_g} \frac{L^2}{C_i} \frac{1}{V_d}$ where the effective dielectric constant of SAND (k_{eff}) is ~3.0, channel length (L) was ~1.5 μ m, SAND thickness (t_{ox}) ~15 nm, and the radius (r) of the In₂O₃ NW was 10 nm. The high transistor performance was mainly attributed to the SAND gate dielectric.

2.7 Optical properties of In₂O₃ nanostructures

It is observed and believed that bulk In₂O₃ does not show PL signal at room temperature.⁵⁶ But there are ample reports on the UV-visible (especially in blue green range) emission of the In₂O₃ nanostructures.^{57, 41} This type of emission has been the subject of many speculations and mainly attributed to the native defects such as oxygen vacancies, indium interstitials with different charged states. The visible emission is dependent on the morphology of the nanostructures, because different morphologies have different amount of oxygen vacancies and indium interstitials, which are inducing the new energy levels in the band gap. These new energy levels provide the recombination centre to the photo-generated hole with electron trapped in the oxygen vacancies. As a result, visible emission is possible in In₂O₃ nanostructures. *Cao et al.*⁵⁷ have reported the room temperature ultra violet emission from

In₂O₃ nanowires. In this report, the PL peak at 398 nm is attributed to the near band edge (NBE) emission. PL emission from In₂O₃ nanostructures at 470 nm is reported by *Guha et al.* and group.⁵⁸ *Wu et al.*⁴¹ have reported at 416 nm from In₂O₃ NWs and at 480 nm and at 520 nm from In₂O₃ nanoparticles.⁵⁹ It has been found that the In₂O₃ samples with oxygen vacancies show electron paramagnetic resonance (EPR) signal which shows the oxygen vacancies are paramagnetic in nature.⁵⁸ The finding is believed to be proving that the oxygen vacancies in In₂O₃ nanoparticles, nanopylramids, and nanocolumns are responsible for PL emission in visible range.^{58, 59} The origin of these PL emissions is still controversial despite the large number of research articles. *Kumar et al.*⁶⁰ have performed a study to understand the origin of PL, by variation of oxygen vacancy concentration in In₂O₃ octahedrons on the basis of EPR and PL signal strength. They have concluded that other than oxygen vacancies, In interstitials related defects also contribute to the PL in In₂O₃ microstructures. This report is in contrary to many other research works where it has been proposed that solely oxygen related defects are involved in the PL emission from MOx nanostructures.⁵⁷⁻⁵⁹

To get a band to band or NBE emission, PL study at low temperature has been performed by several groups. *Mazzera et al.*⁶¹ have performed a temperature dependent PL study from 20 K to 300 K on the In₂O₃ nanowires, and they have observed a broad and complex PL spectrum centered at 420 nm and 630 nm at low temperature. They have attributed the peak at 420 nm to single ionized oxygen vacancy and the peak at 630 nm to the native defects such as interstitial oxygen (O_i), In vacancy (V_{In}) or antisite oxygen (O_{In}). There is no report in best of our knowledge on the band to band or NBE peak below 398 nm.⁵⁷

2.8 Device applications

Among the many possibilities, nanowire-field-effect-transistor (NW-FET) is the potential 1D nanostructure device for chemical and biological sensing and other electrical measurements. These NW-FET based sensors offer numerous advantages on the detection of chemical/biological species. Firstly, nanowires construct the active 1-D channel in a NW-FET device, and the conductance is sensitive to its surrounding environment. Secondly, the direct interaction with the surrounding environment as the nanowire channel is exposed open in NW-FET configuration. Another advantage is in NW-FET the electrical current flows through the confined cross section of the nanowires which can be altered during the chemical sensing. These remarkable characteristics of NW-FET device makes it a highly sensitive device for detection of minute traces of chemical and biological species. In the area of bio-sensing, immobilization of biomolecules on the NW channel tune the conductance of NW. As a result, NW-FETs readily reflect the change in conductance. NW-FETs have the potential to be a highly sensitive device by modulating the active channel volume through the accumulation or depletion of charge carriers during sensing.

2.8.1 Bio-sensor

In the field of bio-sensing, silicon nanowires have been extensively used.⁶² Apart from silicon nanowires, MOx 1D nanostructures have also been explored. In₂O₃ nanowires for biological detection have been employed by *Curreli et al.*⁶³ The In₂O₃ nanowires were first treated by the phosphonic acid solution. Then further immobilization of single-stranded DNA was employed. Currently the research is more towards CNT (carbon nanotube) based biosensors, and there are number of successful reports on the CNT based bio detection.^{64, 65} When we compare CNT with In₂O₃ nanowire; we find them complementary to each other in the electrical properties. CNT based FETs normally show *p*-type transistor characteristics. In

contrast, In_2O_3 based NW-FETs display *n*-type transistor characteristics. Another property where these two materials are complementary to each other is, CNTs are hydrophobic while In_2O_3 NWs are hydrophilic in nature. *Tang et al.*⁶⁵ have done a systematic study of CNT and In_2O_3 nanowire's sensing behavior using low-density lipoprotein (LDL). In spite of 10 fold lower adsorption of LDL molecules on In_2O_3 nanowire than on the CNT, a better response in In_2O_3 nanowire was observed. Apart from the sensors, high performance nanowire transistors can also be fabricated using high quality nanowires.

2.8.2 Gas sensor

In chemical sensing, numerous MOx semiconductors have been found attractive, such as; In_2O_3 , ZnO, SnO₂, TiO₂, Mn₂O₃, CuO, WO₃, V₂O₃, Fe₂O₃, Cr₂O₃, La₂O₃, Nd₂O₃, Co₃O₄, NiO, SrO, GeO₂, Nb₂O₅, Ta₂O₅, MoO₃, CeO₂.⁶⁶ The fundamental sensing mechanism of these materials is connected to the defects present in the material. Atoms or molecules of the detecting gases interact with the oxide surface and prefer to bind at the defect sites (e.g. oxygen vacancy) because of the availability of free electrons.^{67, 68} Oxygen vacancies are electrically and chemically active on most of the MOx surfaces. The electrons left at the vacancy sites, are localized in the energy states closer to the conduction band and behave as donors (*n*-type).⁶⁸ Thus, significant increase in the electron concentration of the MOx occurs. If the testing gas molecules are charge acceptors (oxidizing gases such as NO_x, oxygen, etc.), then the gas molecules use the localized electrons to make the chemical bond to the surface during adsorption, which are available at the vacancy sites. Thus the adsorption of oxidizing gas molecules on *n*-type MOx reduces the conductivity of the material. In contrast, molecules of reducing gases (such as CO, H₂) react with chemisorbed oxygen ions on the surface and remove them. As a result, it creates shallow donor levels and thus

increases the conductivity of the material. Most of the MOx based chemical sensors make use of this property to explain the sensing mechanism.⁶⁹⁻⁷¹

Room Temperature operation

At room temperature, most of the resistive devices (two terminals based) either show very poor response or do not show any response to polluting gases.^{9, 48} At low temperature, response and recovery times are slower mainly because low thermal energy available for the adsorption and desorption. Thus, gas sensors operate at higher temperature (100–500°C) to enhance the surface molecular adsorption and desorption kinetics. Such devices consume high power, increase explosion hazards, and affect the device time and stability. On the other hand, development of room temperature based gas sensors might have important advantages over the high temperature operating devices, such as; low power consumption, reduced explosion hazards, and longer device lifetime and stability. Energy for enhanced adsorption/desorption kinetics can be provided by other means such as ultraviolet (UV) irradiation to generate electron-hole pairs,⁷² or by applying electric field to modulate carrier concentrations.⁷³ The former method has been first demonstrated by *Law et al.* on SnO₂ nanoribbon based gas sensor operating at room-temperature by using UV irradiation to desorb NO₂ gas molecules.⁷² The explanation for UV-assisted desorption of NO₂ was as follows: initially oxygen species adsorb on the SnO₂ nanoribbon surface, consume charge carriers from the n-type SnO₂ nanoribbon and thus create a depletion layer near the surface which extends into the bulk of thin nanoribbon. UV light illumination generates electron-hole pairs in the SnO₂ nanoribbon. The positive holes are consumed by the negatively charged chemisorbed oxygen ions in order to be desorbed. In addition, desorption of

chemisorbed oxygen ions, provide increased adsorption sites which are available for gas molecules which influence adsorption of gas molecules. Produced electron during UV exposure increases the SnO₂ nanoribbon conductivity. Recently, the enhanced gas sensor response of SnO₂ and ZnO nanostructures with UV light irradiation at room temperature is reported.^{74, 75}

The later method to use electric field to enhance adsorption/desorption kinetics was reported by *Fan et al.* in a field-effect transistors (FET) configuration.⁷³ They have reported highly sensitive room temperature chemical sensors for detection of NO₂ and NH₃ gases based upon ZnO nanowire FET.⁷³ A back gated FET configuration was used for such experiment. The field applied modulates the carrier concentration, which in turn significantly affects surface reaction kinetics or gas sensitivity. The sensor device was refreshable by applying a strong negative field by an electro-desorption mechanism.

Catalytic gas sensors

Catalytic reactions on the nanowire surface enhance the sensor response.⁷⁶ The high-effective oxidation catalysts ability of noble metals has been used in enhancement of the surface reactions. Many methods have been used to immobilize the metal particles on to the MOx nanowire surface. Few commonly used methods include impregnation, sputtering, atomic layer deposition (ALD) and thermal evaporation. In literature, many research groups are working on the enhancement of sensor response by means of catalytic activities by using noble metal nanoparticles, such as Au, Ag, Pd, Pt, etc.⁷⁷⁻⁸¹ *Kolmakov and group*⁷⁸ have proposed the mechanism for the Pd catalyzed sensing. They have proposed “electronic” and “chemical” processes to explain the change in the gas sensor response. In the electronic

mechanism, a depletion zone forms around the metal (Pd) nanoparticle which alters the nano-Schottky barriers during gas exposure. The chemical mechanism is based on the highly effective catalytic ability of metal (Pd) nano-particles. The above mentioned chemical process is much often known as spillover effect.⁸² *Kolmakov et al.* have also observed that the catalytic activities greatly depend on the metal coverage on the nanowire surface.⁷⁸

2.8.3 Sensor performance parameters

The important performance parameters for gas sensors are sensor response, response and recovery time, and limit of detection (LOD). There are two types of gases according to the nature of electronic interaction between gas molecules and sensor material *viz.*; oxidizing and reducing. Interaction of oxidizing gases increase the device resistance due to withdrawing nature of gas molecules (e.g. NO₂ and O₃), and interaction of reducing gases increase the device conductance (reduce resistance) due to electron donating nature of the gas molecules (e.g. CO and H₂). In conductometric gas sensors, the sensor response (S) for oxidizing gases is calculated as R_g/R_a , where R_g is the resistance in gas, and R_a is the resistance in air). On the other hand for reducing gases, device's conductance (G) is used in place of R to define S (G_g/G_a). Response (recovery) times are measured as the time taken by the device to undergo resistance/conductance change from 10% (90%) to 90% (10%) of the value in equilibrium (base value) upon exposure to an oxidizing /reducing species.^{9, 83}

2.9 Current status and problems

An ideal gas sensor should possess the following characteristics;

- ✚ high sensitivity, selectivity and stability
- ✚ low operating temperature
- ✚ low power consumption
- ✚ small response and recovery time
- ✚ reproducibility and low cost to meet the demand for mass production

After intense research of last decade, 1D MO_x nanostructures based sensors have improved most of the above mentioned requirements in the sensing of hazardous gases and hydrocarbons. SnO_x based nanostructures have shown an improved sensor response to sub ppb level of CO gas at 200-300°C operating temperature.⁸⁴ On the other hand, Schottky contacted devices have shown enhanced sensor responses for some gases. *Wei et al.* have achieved a high sensitivity of 32 000% by utilizing the Schottky contacts in the device, when operated in reverse bias mode at 275 °C for detection of 400 ppm CO gas.⁸⁵ This improvement is 4 orders of magnitude higher in comparison to an Ohmic contact device under the similar working conditions.⁸⁵ Metal additives have been also used to improve the sensor response.^{86, 79} Most of these sensors are operated above room temperature in order to obtain a high sensor response.

High working temperature is needed to obtain a high sensor response for most of the commercial SnO₂ and ZrO₂ thin film based resistive gas sensors. However, researches have been carried out including doping of different elements and metal nanoparticle functionalization to improve the sensor response and selectivity at lower working temperature.

Although a large number of 1D MO_x based sensors are found to be sensitive to the different gases such as; NO_x, CO, CO₂, O₂, NH₃, H₂S, O₃, H₂, alcoholic vapors, acetone etc.,

some problems still need to be solved such as room temperature operation, poor selectivity, stability and reproducibility. There are few areas that require attention, in order to meet the expectations;

- Fundamental studies for better understanding of the surface kinetic reactions of the gas molecules with the sensor material
- Design of the new nanostructures based material systems
- Incorporation of materials with specific catalytic properties to enhance the selectivity.
- Sensor fabrication and manufacturing techniques for the nanostructures based material systems
- Sensor geometry based on nanostructures to reduce the operating temperature.

Chapter 3

Experimental Methodology

In this chapter, the description of the experimental methodology used for the growth and device fabrication of quasi 1D nanostructures are presented briefly. The detailed experimental methodology is presented in the corresponding chapters. The main experimental steps are categorized as follows;

- ❖ Growth of undoped and Zn- doped In_2O_3 nanowires followed by hetero-structured nanowire growth.
- ❖ Morphological and microstructure characterization of the as grown nanostructures including X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS).
- ❖ Resistor and FET based device fabrication using single and network of nanowires.
- ❖ Electrical and sensing characterizations on undoped, Zn-doped and hetero-structured In_2O_3 nanowires devices.

3.1 Growth of nanostructures

Quasi 1D MO_x nanostructures were prepared using evaporation-condensation technique, with VLS growth mechanism promoted by the use of metal nanoparticles as catalyst.⁹ In this work, Au nanoparticles has been used as the catalyst for the nanowire growth.

3.1.1 Growth of In_2O_3 nanowires and layered nanorods

In_2O_3 nanowires and nanorods were prepared in a horizontal tube furnace under argon gas flow. In this work, different nanostructures were synthesized by variation in the working parameters during growth such as growth temperature, gas flow rate and pressure inside the tube. A molar ratio 1:3 of In_2O_3 powder and carbon powder respectively was mixed thoroughly in a horizontal ball mill for 4 hours. The source and the Si substrates with a gold layer (the layer thickness is mentioned in the respective growth section, typically ~9 nm) were placed downstream in the small quartz tube. The source temperature was varied from 875°C to 1000°C in different deposition processes. Growth time was varied from 5 min to 60 min and argon flow rate was varied from 10 - 60 sccm (standard cubic centimeter) in different depositions, and accordingly different nanostructures were obtained. Only one parameter was changed at one time in order to study its effect on the growing structures. The schematic drawing of the experimental setup for the growth of nanowires is shown in the Figure 3.1.

Figure 3.1 Schematic diagram of the horizontal double tube CVD furnace for nanowire growth.

3.1.2 Growth of Zn-doped In₂O₃ nanowires

Zn-doped In₂O₃ nanowires were synthesized in a horizontal CVD double tube furnace at a source temperature of 900°C. The source for the growth was used as a mixture of ZnO and In₂O₃ powders mixed with graphite powder. Argon flow rate was fixed at 50 sccm during the deposition, and the pressure inside the furnace was maintained at 1 mbar. Si substrates with ~9 nm Au catalyst layer were placed downstream and the substrate temperature ranges from 400-550°C with deposition duration of 1 hr.

3.1.3 Growth of In₂O₃-ZnO core-shell nanostructure

In₂O₃-ZnO core-shell nanowires were synthesized in the same horizontal double tube VLS furnace in a two-step growth process. In the first step, core In₂O₃ nanowires were synthesized at 900°C source temperature using 9 nm gold layer as catalyst for the nanowire growth with growth duration of 30 min. In the second step, a smaller growth duration of 5 min was used for the growth of the ZnO shell on the In₂O₃ core without catalyst. The source temperature and the argon flow rate were kept constant at 900°C and 50 sccm respectively, as in the first step. Final products on the alumina substrate were collected near the cooler end (450-500°C) of the tube.

3.2 Morphological and micro-structural characterizations

Morphological and micro structural characterizations of the as-grown products were performed to study the composition and crystallinity of the nanostructure. A Rigaku X-ray diffractometer using CuK_α radiation with thin film attachment was used to collect the X-ray

diffraction (XRD) patterns. The 2θ -value was scanned from 20° to 70° with scan a rate of $0.02^\circ/\text{second}$ and the X-ray machine was operated at 40 kV and 40 mA. The as deposited samples were studied under FESEM on a JEOL 6340F and JEOL 7600F scanning electron microscope operated at 5 kV. A JEOL JEM 2010 microscope at an accelerating voltage of 200 kV was used to collect the high resolution transmission electron micrographs (HRTEM) and the selected area diffraction (SAD) patterns. JEOL JEM 2100F TEM was used to perform energy dispersive x-ray (EDX) analysis on a single nanowire. A Cary Eclipse EL spectrometer at an excitation wavelength of 264 nm was used to study the PL of the nanostructures at room temperature on. Surface potential profile of a single nanowire was obtained by KPFM method in a NT-MDT NTEGRA EC configuration scanning probe microscope at room temperature.

Raman spectroscopy was performed using a WITec CRM 200 spectrometer. The instrument was equipped with a laser of wavelength 488 nm and an output power of 50 mW. Raman spectra were recorded using the 100x objective lens. All spectra were recorded between 100 and 1600 cm^{-1} .

3.3 Device fabrication

We have mainly fabricated two types of devices; the first type is single nanowire based FET devices and the second type is nanowire network based resistor devices. A highly doped n-type silicon wafer with a 60 nm SiN_x high-k dielectric layer was used to study the single nanowire-based devices. The contact electrodes were defined by the standard optical-lithography followed by Cr/Au (10/50 nm) deposition and liftoff. A global back gate of

highly conductive Si substrate (resistivity 0.005 Ω -cm) was used in all devices. In₂O₃ nanowires dispersed in isopropyl alcohol (IPA) solution was prepared and drop-casted onto the Si substrate. The nanowire alignment method is described in the following sub-section. The nanowire network resistor devices were fabricated on alumina substrate. As deposited nanowire samples were contacted by metal electrodes at the two ends of the substrate. Comb shaped electrodes pair were patterned with a channel length of 100 μ m to flow the current across the nanowire network. A heater was fabricated at the back of each substrate for the precise heating of the device. The selection of substrate for the sensor platform plays an important role especially in higher temperature operations. Higher working temperature can produce leakage through the substrate which deteriorates the sensor response. So it is useful to use a poor electronic conducting substrate with high thermal conductivity (e.g. alumina) for the high working temperature resistor based devices.

3.3.1 Nanowire alignment: One of the most critical issues to fabricate the nanoelectronic devices is to place the nanostructure precisely at desired location. The nanowire alignment can be done in two ways: firstly, align the nanowire first by using Langmuir Blodgett (LB) technique,⁸⁷ roll transfer printing^{88, 89} or fluidic⁹⁰ technique and then deposit the source – drain on top of the nanostructure. Second method is, manipulate using dielectrophoresis (DEP)⁹¹ onto predefined source and drain electrodes. Among these methods, DEP has been widely explored to manipulate nanowires. DEP possesses several advantages such as, easy to operate, economical and highly efficient method. In DEP, electric field is applied between two electrodes where nanowire is forced to align. Both DC and AC fields can be applied to align the nanostructure. *Duan et al*⁹² manipulated InP nanowire under DC electric field. It has been reported that density of aligned nanostructures mainly

depends on the magnitude of the applied electric field.^{93, 94} Other important parameters such as magnitude and frequency of the applied field, geometry of microelectrodes must be carefully controlled to place nanostructures precisely at desired locations. *Chen et al.* reported that orientation of the nanowires is strongly depending on the magnitude as well as on frequency of the applied field.⁹³ In addition, *Liu et al.* showed the alignment dependence on the geometries of both the microelectrodes and the NWs.⁹⁵

Now we present the DEP alignment results and optimization of the technique used for the fabrication of device by aligning single nanowire between source-drain. We have measured the effect of the concentration of the nanowire suspension, the magnitude and frequency of the applied field.

3.3.1.1 Nanowire-suspension

Preparing nanowire suspension is a very important step is the alignment of nanowire using DEP. Figure 3.2 shows the effect of concentration of the nanowire suspension. As the concentration of suspension increases, more nanowires aligned between source-drain. Nanowires agglomerate in the suspension at higher concentration which creates difficulties in the fabrication of single nanowire device. The suspension was prepared by ultra-sonication method. Different concentrations were obtained by increasing the solvent volume for the same solute amount. The various suspensions conditions are summarized in Table 3.1 and their corresponding SEM images are shown in Figure 3.2.

Table 3.1 Concentration variation for different samples:

S.N.	Sample name	Concentration (g/L)
1	a	0.10
2	b	0.05
3	c	0.0033
4	d	0.0025

Figure 3.2 Effect of concentration of nanowire suspension on alignment; (a) 0.10 g/L, (b) 0.05 g/L, (c) 0.0033 g/L and (d) 0.0025g/L.

Figure 3.2(a) shows SEM image of sample (a) in which 4-5 nanowires are aligned, forming multiple nanowire device and the nanowire agglomeration can be observed. With decreasing concentration of nanowire suspension, single nanowire aligned devices were easily obtainable. This can be clearly observed from Figure 3.2(d). Hence, an optimum concentration should be selected to make nanowire suspension.

3.3.1.2 Effect of applied voltage

Alignment of nanowires strongly depends on the magnitude of voltage applied or electric field. By increasing the DC or AC bias electric field, more nanowires are attracted towards the electrode. With the increase of voltage or electric field, nanowires experience larger force which increases the yield of aligned nanowires. Figure 3.3 depicts the result of voltage variation, with increased voltage the alignment increases. Hence to have a single nanowire device, we should have an optimum electric field or applied voltage to align the nanowire.

Table 3.2 Effect of voltage variation on nanowire alignment for different samples:

S/ N	Sample name	Magnitude of voltage bias (V)
1	a	6
2	b	10
3	c	12
4	d	14

Figure 3.3 Effect of magnitude of applied voltage on nanowire alignment; (a) 6 V, (b) 10 V, (c) 12 V and (d) 14 V.

3.3.1.3 Effect of frequency

Frequency plays a very critical role in the alignment of nanowire. Similar to the concentration and voltage variation methods, we have measured the effect of frequency on the nanowire alignment. With increased frequency (from 50 KHz to 400 KHz), the nanowire alignment was found to be increased. This effect may be due to the dominating DEP force in the system.⁹⁶

3.4 Electrical and sensing characterizations

Electrical and sensing studies on the NW-FET were performed on Keithley 4200-SCS. Keithley 4200-SCS semiconductor characterization system was equipped with an optical microscope and sensing gases with gas controller. Sensing test was performed on a number of pollutant and explosive gases including; nitrogen gas, nitric oxide (NO), nitrogen dioxide (NO₂), carbon mono-oxide (CO), hydrogen, ethanol and acetone gases. The responses of the NW-FET to different gases were analyzed by measuring the resistance/conductance change upon exposure. The schematic layout of the sensing setup is shown in Figure 3.4. Current was measured at a fixed voltage and at a fixed humidity of 50 %. The overall gas flow rate in the chamber was kept constant at 300 sccm during all sensing experiments. Various concentrations were obtained by diluting a premixed concentration of gas in air/N₂.

The sensor response (S) of the gas sensing device was calculated as;

$S = R_g/R_a$ was used for oxidizing gases and

$S = G_f/G_i$ was used for reducing gases.

-where R_a & R_g are the resistances of the device in air and testing gas respectively and G_i and G_f are the initial and final (after gas exposure) conductances of the device respectively.

Figure 3.4 Schematic diagram of the sensing setup.

Chapter 4

Synthesis and Characterization of Quasi 1D In₂O₃ Nanostructures

In this chapter, synthesis and microscopic characterizations of quasi 1D In₂O₃ based nanostructures are presented. In₂O₃ nanowires, nanotowers, long layered nanorods, rectangular cross sectional nanorod and hierarchical hetero-nanostructures are grown using carbothermal reduction of In₂O₃ powder by varying source temperature in a CVD horizontal furnace. At 875°C-910°C source temperature, In₂O₃ nanowires were formed by VLS mechanism. Due to high saturation vapor pressure, the growth is believed to be changed to VS initiated growth on the substrate surface when source temperature is raised to 950°C. Meanwhile, alternate VLS-VS grown nanotowers can be obtained at the bottom of the substrates. Growth of the 1D nanostructures with different morphologies and variation in growth mechanism from a single precursor with the confinement of vapor pressure enables the diversity of In₂O₃ nanostructure synthesis. The main aim of synthesizing different nanostructures is to explore gas sensing properties by variation in morphology of the sensing material. We have mainly studied the nanostructures which are suitable to enhance the sensing performance at room temperature on a single nanostructure device configuration. We have grown various nanostructures of In₂O₃ to study the growth mechanism at various

growth conditions, with a purpose of optimizing the dimension and yield for gas sensors in the later chapters.

4.1 Introduction

1D nanostructured systems have attracted much research attention recently due to their novel properties and wide applications. Semiconducting oxide nanowires such as ZnO, In₂O₃ and SnO₂ have become increasingly important parallel to the success with group IV and III-V compound semiconductor nanowires. Amongst many MO_x, In₂O₃ is an important n-type wide direct band gap transparent semiconductor with wide range of technological applications in optoelectronic devices and transparent chemical & bio- sensors^{14, 65} oxide based TFTs,¹² and solar cells.⁹⁷ High crystalline quality In₂O₃ nanostructures are therefore required preferentially in single crystalline form, for studies of their electronic properties and potential applications in sensing, nanoscale transistors and light emitting diodes.^{55, 16}

Many growth and synthesis methods to produce 1D semiconducting nanostructures have been explored including, vapor-phase transport,^{46, 41, 98, 42} pulsed-laser deposition,⁹⁹ and electrochemical deposition.¹⁰⁰ Vapor-phase transport is a potential method among the other synthesis methods to produce high crystalline quality nanostructures. In this route, by changing the experimental conditions the morphologies of growing nanostructures can be modulated. Therefore it is important to study the effect of the experimental conditions and the morphologies.

4.2 Experimental Details

Various In₂O₃ nanostructures were produced using a small one end closed quartz tube of diameter 1.3 cm in a horizontal tube furnace under Ar gas flow (schematic diagram is shown

in chapter 3, where the closed end of the smaller tube was facing the argon gas flow direction). A molar ratio 1:3 of In_2O_3 powder and graphite powder respectively was ball milled in a horizontal ball mill for 4 hrs to mix it thoroughly. The source and the Si (100) substrates with 9 nm gold layer were placed downstream in the quartz tube. All the nanostructures were synthesized under a slight variation in the growth temperature. In the first experiment, the source was heated at 875°C and in the second experiment, the source was heated at 950°C , keeping other parameters constant for both experiments. The furnace heating rates in both the experiments were kept fixed at $15^\circ\text{C}/\text{min}$ under 60 sccm (standard cubic centimeter) flow rate of Ar gas and the furnace was operated at 1 mbar.

The final yellow colored products were collected near the cooler end ($450\text{-}500^\circ\text{C}$) of the tube. XRD patterns were collected using CuK_α radiation on a Rigaku X-ray diffractometer with thin film attachment. The morphology of the samples were studied by FESEM on a JEOL 6340F scanning electron microscope which was operated at 5 kV. HRTEM and the SAD patterns were collected using a JEOL JEM 2010 microscope at an accelerating voltage of 200 kV. EDX analysis on single nanowire was performed on JEOL JEM 2100F. The optical characterizations were performed on SHIMADZU UV- 2501 PC spectrometer. Raman spectroscopy was performed using a WITec CRM 200 spectrometer. The instrument was equipped with a laser of wavelength 488 nm and an output power of 50 mW.

4.3 Result and Discussion

In a small quartz tube under confined conditions of In vapors, a slight change in the source temperature made a significant change in the diameter and morphology of the growing

nanostructures. The insertion of smaller quartz tube made a significant change in the growing species by confining the reactants in a smaller volume. We managed to carefully control the morphologies of the growing nanostructures after using the smaller quartz tube. The products grown in experiment I at source temperature of 875°C are shown in SEM image in Figure 4.1, which were found to be consisting of small diameter nanowires with circular cross section (20 nm to 90 nm as shown in Figure 4.1a & b).

The XRD pattern in Figure 4.2 was obtained from the as grown products in experiment I. All the XRD peaks were indexed to cubic In_2O_3 crystal system with a lattice parameter of $a = 10.118 \text{ \AA}$ (JCPDS card no. 00-06-0416). Moreover, no other impurities (e.g. In or other phases) peak were detected.

A typical TEM image of the In_2O_3 nanowire (diameter ~50 nm) revealing the general morphology grown by VLS mechanism is shown in Figure 4.3(a). EDS analysis on the single nanowire (in Figure 4.3a) indicates that the nanoparticle on the apex mainly consists of gold and trace amount of In and O elements, while the stem of the nanowire consisted of In and O elements. The presence of the gold at the apex of nanowire confirms the VLS mechanism growth process. HRTEM image of the In_2O_3 nanowire in Figure 4.3(b) shows growth dominated along $\langle 111 \rangle$ which is in agreement with the XRD results. The measured distance (between adjacent planes) in the growth direction is $2.94 \text{ \AA}$, which is close to the calculated value from XRD, confirming the nanowires dominantly grew along $\langle 111 \rangle$ direction ($d_{222} = 2.92 \text{ \AA}$).

Figure 4.1 (a) Low and (b) high magnification FESEM images of In_2O_3 nanowires deposited at a source temperature of 875°C . The scale bar in the inset of Figure (b) is 200 nm.

Figure 4.2 X-ray diffraction pattern of the In_2O_3 nanowires grown at 875°C .

Figure 4.3(a) Low magnification TEM image of single In_2O_3 nanowire consisting Au at its apex with EDS analysis of the tip and stem of the nanowire and (b) shows the HRTEM image of the In_2O_3 nanowire with the lattice spacing of 0.32 nm. Inset shows the electron diffraction pattern measured along the [101] zone axis.

All the above characterizations from FESEM, TEM and EDS, were consistent with the proposed mechanism of VLS growth for nanowires formation, indicating that gold nanoparticles functioned as a catalyst in In_2O_3 nanowire growth.

The experiment II was operated at a source temperature of 950°C, two types of nanostructures on the same substrate were observed. The first type of the nanostructures was nanotowers (~ 10 µm long) with gold particles on the top. These nanotowers were mostly located in the background (Figure 4.4a & b). A high magnified FESEM image of the stem of the product is shown in the inset of Figure 4.4(b) which is made of truncated octahedral nanostructures with gold on the top. Second type of nanostructures was found longer (20 to 50 µm) nanorods with layered (truncated octahedrons) structures. These nanostructures consist of imperfect octahedral top (Figure 4.4c & d) and were mostly located in the foreground. The corresponding HRTEM images are shown in Figure 4.4(e & f). The jagged edges of the ultra-long layered nanorods found at the foreground in the products resultant from higher source temperature (experiment II). The diameter of the nanorod is found to be uniform along the length without tapering.

It is important to note that, in both the experiments, argon gas is not playing a carrier gas role. Instead it controls the oxygen partial pressure inside the quartz tubes. The transport of the reagent species from source to substrate was realized due to pressure difference between close and open ends of the smaller tube while evaporation of the In vapors occurred as a result of carbothermal reduction of In₂O₃ powder. Due to the smaller volume of the quartz tube, a higher In vapor saturation inside the tube was maintained.

4.3.1 Growth mechanism of the formation of nanostructures:

The In₂O₃ nanostructures growth may involve the following steps:

Step I- In₂O₃ powder reduced into metallic In vapors and CO when reacted with carbon powder at a higher temperature.

Step II- Formation of In_2O_3 by the oxidation of metal In vapor.

In our experiments, although oxygen was not added intentionally, we believe that the oxygen for the 2nd step of the above reaction came from atmospheric residue oxygen inside the tube (as only rotary pump was used to evacuate the tube) and leakage of the system which can be controlled consistently. In our VLS system, the Ar gas does not play a carrier gas role as in conventional VLS growth, instead it indirectly affects the transportation of the precursors from source to the substrates. When carbothermal reduction of In_2O_3 powder into In and O starts at a particular temperature the pressure inside the smaller tube increases. As a result, a pressure difference creates between the close and open end of the smaller tube, due to which transportation of the precursors from source to the substrates takes place and the In vapors condense on the substrate at lower temperature end of the tube.

Figure 4.4 As synthesized (at 950°C) images of, (a) background nanotowers under low magnification, (b) nanotowers under high magnification FESEM and the inset shows tip of the nanotower with gold on top (scale bar in the inset is 100 nm), (c) foreground long nanorods, (d) long layered nanorods under high magnification FESEM, inset shows the octahedral cap and body of layered nanorod, the scale bar in the inset is 150 nm. Figure (e) and (f) show the low and HRTEM image of the layer structured nanorod respectively.

4.3.1.1 Formation of layered nanorod: After in depth characterizations, the uniform long layered nanorods located at the foreground were observed without having Au nanoparticle at the apex. We attribute the initiation of growth of such nanorods is based on VS growth mechanism. At 500°C (the substrate temperature), it is believed that the Au droplets sizes on the silicon substrate were not uniform. There may be some bare places exist on the silicon substrates where no Au droplet has formed. On such bare locations (where there were no Au droplets), with sufficient In vapors a nucleation without catalyst has occurred. This process initiates nucleation without catalyst droplet and led by VS mechanism. The one-end closed smaller quartz tube has helped to confine the In vapors in a smaller volume and increase the saturation of the reagent species. The confined volume of reagent species made possible the nucleation without catalyst droplet. We have obtained high yield with dense and long layered nanorods under such confined conditions of high In vapor pressure.

The step by step growth process of such kinds of layered nanorods is illustrated in Figure 4.5(a). To explain the formation of these layered nanorods with octahedral top, we have adopted a bottom growth mechanism.⁴² At stage I, an In rich particle forms on the Si substrate under a high In vapor super saturation in confined conditions of the In vapors at 950°C.

Figure 4.5 Schematics of the growth mechanisms of, (a) step by step growth of the layered nanorod located at the foreground with octahedral cap on the apex; stage I: formation of In rich particle; stage II: re-evaporation of In in the particle and the following growth resulted in the truncated octahedron; stage III: 1-D growth of the stem induced by truncated octahedron; stage IV: formation of the octahedral stem due to the diffusion of the reagent species from side faces of the newly grown 1-D segment; stage V: continuous growth resulting in the formation of the long layered nanorod. Figure (b) shows the step by step growth of the nanotower located at the background with gold droplet on top. Stage I: formation of eutectic droplet; stage II: nucleation and 1-D growth controlled by the catalyst droplet; stage III: formation of the octahedron due to diffusion of the atoms from the side faces of the newly grown 1-D segment; stage IV: growth of the nanotower; stage V: continuous growth resulting in the formation of nanotower.

At stage II, the low melting point In (156°C) inside the particle would re-vaporize and adsorbed on the particle surface. This, together with the adsorbed species transported from the vapor phase, will maintain the growth of the particle. At stage III, as the reaction went on, abundant reagent species adsorbed onto the truncated octahedron. The low energy planes such as (111) were terminated earlier compared to the high energy planes such as (100). As the growth of a plane is related to its energy, thus the low energy planes may grow very slow or even stopped very early. As the reaction progresses, most of the adsorbed species would transfer to the (100) plane to maintain the 1-D growth along the $\langle 100 \rangle$ crystalline direction. The In rich bottom plane (100) will induce the growth of the rectangular stem, confined by the rectangular bottom plane. Stage IV is the major difference compared to reference.⁴² At stage IV, a lateral growth starts from the side faces of the newly grown 1-D segment (which was formed in stage III) due to the high saturation of the In vapors under confined conditions in this experiment. Such layered segments along the length of the rod would repeatedly form after the availability of the next new 1-D segments. At the last stage (stage V), the growth terminates due to the end of carbothermal reaction (either due to the consumption of source material or end of preset time duration). As a result, the formation of long layered nanorod takes place.

4.3.1.2 Formation of the nanotower: Catalyst (gold) nanoparticles were located on the top of shorter length nanotowers (inset of Figure 4.4b) which were located in the background, indicating that the involvement of VLS mechanism in 1-D growth. At the locations where Au droplets were available on the silicon substrate, VLS initiated growth started. Both types of nanostructures (long layered nanorods in foreground and nanotowers at background) were present on the same substrate with relatively high yield.

Nanotowers were observed to be uniform in thickness along the length with truncated octahedron. The formation of the periodical octahedron along the length can be explained by alternate 1-D and 0-D growth, where 0-D growth is controlled by a VS mechanism and 1-D growth is controlled by VLS mechanism. In the literature, *Yan et al.*⁹⁸ have explained the growth mechanism for similar types of nanostructures using a modified alternating VS and VLS growth mechanism.

In comparison to *Yan et al.*⁹⁸, we have obtained higher yield and there are appreciable differences in the dimensions of the nanostructures (these nanotowers are smaller in dimension) and therefore the growth mechanism. Figures 4.5(b) illustrates the step by step growth for the nanotowers. At stage I, when temperature reaches at 950°C, formation of eutectic droplet of In and Au takes place. In the stage II, the nucleation followed by 1-D growth controlled by VLS mechanism starts. As the reaction went on, more In vapors diffuse through the Au droplet. Lateral growth starts at the stage III from the newly formed 1-D segment, accorded with the 0-D growth. It leads to an octahedral configuration due to different growth rates of the different planes under high In vapor saturation. 0-D growth restarted again at stage IV when the reagents species started incorporating again through the lateral surfaces of the newly formed 1-D segment. It creates a new segment of the nanotower. Growth continues at stage V, until the In vapors available from the carbothermal reduction. The carbothermal reduction of In decreases towards the end when temperature starts decreasing (due to preset time duration). As a result, less In vapors are available around the Au droplet. Towards the end, under such experimental conditions, only 1-D growth takes place, which leaves behind a sharp tip.

In all the above discussed growth processes 1-D growth was continuous and 0-D growth was periodical along the length. This is opposite to the mechanism reported by *Yan et al.*⁹⁸ where 1-D growth was found periodic and 0-D growth was continuous due to low saturation of the In vapors. This difference is attributed to the higher In vapor pressure in our experiment. Another difference is the nanotowers in our case are almost uniform along the length, whereas the reported nanotowers by *Yan et al.*⁹⁸ were found tapered due to the continuous 0-D growth for longer time period. In our work, the uniform diameter could be due to the following reasons; (1) formation of highly dense nanostructures which hindered the reagent species to reach to the lower part of the tower, and (2) the nanotowers are located in the background which face another hindrance from the long layered nanorods located in the foreground.

The temperature dependent nature of the carbothermal reaction has played a crucial role in defining the morphology and diameter of the nanostructures. Indium vapor pressure increases at higher source temperature mainly due to the higher carbothermal reduction process. It leads to the availability of higher In vapors around Au droplets on the substrate. As a result, lateral growth (0-D) led by VS mechanism starts. Another effect of higher source temperature is the Au droplets agglomerated to form a larger droplet, which contributes to the non-uniform distribution of the Au droplets on the Si substrate. It leaves behind the bare places (without Au droplets) on the Si substrate where layered nanorods nucleated led by VS growth (as discussed previously). In the experiment I, which was conducted at a lower source temperature of 875°C, negligible lateral growth of nanostructures was observed. The surface was found rough in atomic scale and a very small lateral growth was observed under HRTEM imaging (Figure 4.3b). We believe that at lower source temperature (875°C), the In

vapor pressure inside the smaller quartz tube was not large enough to start a lateral growth. As a result, only 1-D growth led by VLS mechanism was observed.

Other 1-D nanostructures such as; rectangular nanorods (Figure 4.6), dendritic 1-D nanostructures and hierarchical nanostructures (Figure 4.7) were successfully grown by varying the growth parameters.

Figure 4.6 Rectangular cross sectional 1D nanostructures, (a) & (b) show the FESEM images of the as grown nanostructures and (c) shows the HRTEM image.

Rectangular cross sectional nanostructures as shown in Figure 4.6 were grown using VS mechanism at a higher source temperature of 1000°C without using any catalyst. At high source temperature, the carbothermal reduction of In_2O_3 into In would increase the deposition rate of the nanostructure. As a result rectangular cross section was obtained due to the cubic In_2O_3 crystal system.

Figure 4.7 FESEM images of, (a) & (b) low and high magnification images of dendritic nanostructures, (c) & (d) low and high magnification images of hierarchical In_2O_3 nanostructures, respectively.

The dendritic nanostructures were grown on a scratched Si substrate without using any catalyst (Figure 4.7a & b). The sizes of the nanostructures were observed to be controlled by the size of the scratch on the substrates. The shapes of the nanostructures were found imitating the shape of the scratch on the substrate which can be controlled by the size of the scratch. The hierarchical nanostructures were grown in two step growth (Figure 4.7c & d). In the first step, In_2O_3 nanowires were grown as described previously by VLS method. In the second step, 20 min growth duration was used for the secondary arm growth via VS mechanism without using any catalyst. Random secondary arms were observed due to the

random nucleation of the In_2O_3 on the core nanowire. Such nanowires with sharp secondary arm tips are applicable in the field emission. We have summarized the growth details in the following Table 4.1:

Table 4.1 Summary of the growth details of different nanostructures:

S/N	Nanostructure	Source	Source Temperature (°C)	Substrate Temperature (°C)	Pressure
1.	Nanowires	$\text{In}_2\text{O}_3 + \text{C}$ (3:1)	875-910	450-500	1 mbar
2.	Layered nanorods	$\text{In}_2\text{O}_3 + \text{C}$ (3:1)	950	450-500	1 mbar
3.	Rectangular nanorods	$\text{In}_2\text{O}_3 + \text{C}$ (3:1)	1000	450-500	1 mbar
4.	Dendritic nanostructures	$\text{In}_2\text{O}_3 + \text{C}$ (3:1)	950	450-500 (on scratched Si substrate)	1 mbar
5.	Hierarchical In_2O_3 nanostructures	$\text{In}_2\text{O}_3 + \text{C}$ (3:1)	950 (two step growth)	450-500	1 mbar

4.3.2 Optical Characterizations

Optical properties of nanowires with circular cross section grown at a source temperature of 900°C, were studied by photoluminescence (PL), ultraviolet-visible (UV-VIS) and Raman spectroscopy methods. It is well known that bulk In_2O_3 has no light emission at room temperature.⁵⁶ Recently many groups have reported photoluminescence emission from In_2O_3 nanostructures; nanoparticles,⁵⁹ nanofibres, and nanowires.¹⁰¹ Figure 4.8 shows the PL emission spectrum measured from pure In_2O_3 nanowire by using an excitation wavelength of 325 nm at room temperature. A series of peaks from 525 nm to 680 nm was observed which was centered at ~620 nm. In literature, most of the PL peaks from MOx are attributed to the impurities such as oxygen vacancies, metal interstitials and surface states present in the

nanostructures. Different morphologies of nanostructures contain different oxygen vacancies, as a result PL varies with morphology and nanostructure synthesis conditions. At 325 nm excitation wavelength, our nanowire samples do not show any UV emission. Similar PL emission peaks at 530 nm and 555 nm were reported from In_2O_3 octahedron when excited at 325 nm.¹⁰² These peaks were attributed to oxygen vacancies. PL peak at 670 nm is reported from In_2O_3 nanowires at low temperature (10 K) when excited at 325 nm and attributed to oxygen vacancies.¹⁰³ A PL emission spectrum centered at ~600 nm from In_2O_3 octahedrons is attributed to the metal interstitials.⁶⁰ In literature, there are several reports on the PL emission of MO_x and all peaks are attributed to different types of defects from different morphologies. A similar PL emission profile with a peak centered at ~570 nm with a shoulder at ~630 nm from In_2O_3 nanobelts were reported by Jeong *et al.*¹⁰⁴

Figure 4.8 PL emission spectrum measured from pure In_2O_3 nanowire, at an excitation source wave length of 325 nm at room temperature.

UV-VIS spectroscopy was performed on Shimadzu UV- 2501 PC model. For the evaluation of band gap energy UV-VIS spectrophotometry equipped with diffuse reflectance accessory is being used very often. Figures 4.9(a) show the diffuse reflectance spectra (DRS) of In_2O_3 . The DRS of pure In_2O_3 shows maximum transparency in the visible range of the light. The estimated band gap value of pure In_2O_3 is ~ 3.75 eV (Figure 4.9b).

Figure 4.9(a) Diffuse Reflectance Spectrum of In_2O_3 nanowires, (b) $(K h\nu)^{1/2}$ as a function of energy of In_2O_3 nanowires.

Figure 4.10 Raman pattern measured from In₂O₃ nanowires at room temperature.

Raman scattering was performed on the as deposited and undoped In₂O₃ sample and the result is shown in Figure 4.10. In the range of 100–1600 cm⁻¹, we observed five sharp Raman scattering peaks at 135.5, 307.5, 368.5, 494.5, and 630.5 cm⁻¹, whose position and intensities are the characteristics of the standard Raman spectra for In₂O₃.¹⁰⁵ The presence of defects on the nanostructures and the crystallinity of the grown products can have profound influence on the Raman spectra. Some slight shift in peak positions was observed and is attributed to the defects (oxygen vacancies and/or indium interstitials) present in the nanostructures which we have also observed in the photoluminescence measurement. The Raman peak at 307 cm⁻¹ is related to the stretching mode of the indium oxide and is sensitive to the oxygen vacancies.⁶⁰ The strong peak at 307.5 cm⁻¹ in our sample indicates the products are oxygen deficient which supports the findings from the PL analysis of the products.

4.4 Summary

In summary, single crystalline, cubic In_2O_3 nanowires, long layered nanorods and nanotowers were successfully synthesized on a Si substrate by varying the deposition temperature. Other nanostructures such as; rectangular cross sectional nanorods, dendritic nanostructures and hierarchical nanostructures were synthesized by varying the growth parameters. The morphology and diameter of the growing nanostructures were tuned by adjusting the growth temperature under confined conditions of the In vapors in a small quartz tube. VS - VLS alternative growth resulted in the formation of small nanotowers with truncated octahedrons mainly located in the background. The confinement of In vapors in a smaller volume provides higher In vapor pressure which serves to initiate lateral growth. Optical characterizations on the as grown In_2O_3 nanostructures show the oxygen deficient nature of the as grown nanostructures which is essential for the sensing application.

Chapter 5

Nanowires Network Resistor Based Chemical Sensors

In this chapter, nanowires network resistor based sensors have been explored toward different pollutant gases. Pristine In_2O_3 , In_2O_3 -ZnO core-shell nanowires and Zn-doped In_2O_3 nanowires are tested for different gases. This chapter is mainly divided into two major sections; first section describes the In_2O_3 -ZnO core-shell nanowires and second section deals with Zn-doped In_2O_3 nanowire based gas sensors. Different pollutant gases such as; CO, NOx, H_2 , acetone, and ethanol were tested on pristine In_2O_3 , In_2O_3 -ZnO core-shell and Zn-doped In_2O_3 nanowire. A comparison of the gas sensing response of each sensor with the pristine In_2O_3 nanowires is presented. The gas sensing mechanism of these hetero-structured nanowires is discussed in detail.

5.1 In_2O_3 -ZnO core-shell nanowires for chemical sensors

5.1.1 Introduction

Hetero-structured 1D nano-materials have received huge research attention owing their unique properties in nano regime. Hetero-structured materials have shown more versatile functions compared to their monolithic nano-materials counterpart when used for nano-scale devices.¹⁰⁶⁻¹¹² Various hetero structured MOx nanomaterials are synthesized by combined vapor-liquid-solid (VLS) and vapor-solid (VS) condensation: core-shell,¹¹³ core- multi-shell,¹¹⁰ longitudinal,¹¹⁴ and branched hetero-structures.¹¹⁵ The hetero-structures are being

strongly investigated for its functional properties arising from the interconnected junctions. Amongst the other hetero structures, core-shell nano-structures have been found attractive in chemical sensors.¹¹⁶⁻¹²⁴ Hetero-structures of $\text{SnO}_2\text{-ZnO}$, ZnO-ZnS , ZnO-CdS and CuO-SnO_2 (p-n junction nanorods) were applied as O_2 , NO_2 , NH_3 and H_2S gas sensors.^{118-121, 123, 124} In the chemical sensing, the hetero-structured based chemical sensors have shown a superior response when compared to a pristine material based chemical sensors. ZnO-CdS core-shell nanocables have shown enhanced sensitivity towards NH_3 .¹¹⁹ The better sensor response of ZnO-CdS core-shell nanocables was attributed to the increased surface area and hybrid properties of ZnO-CdS core-shell nanocables after CdS shell deposition on ZnO nanorods.¹¹⁹ A three step hydrothermal synthesis method of $\alpha\text{-Fe}_2\text{O}_3\text{-ZnO}$ core-shell nanorods was used by *Zhu et al.* which dramatically improved the sensitivity for ethanol detection when compared to the pristine $\alpha\text{-Fe}_2\text{O}_3$ nanorods.¹²⁴

A sensor device composed of nanowires with a single crystalline core and a polycrystalline shell possesses advantages over devices made of monolithic nanowires or polycrystalline thin films. Such core-shell nanowires enhance both receptor and transducer functions of the device. For example, the polycrystalline outer shell creates more adsorbing sites for gas molecules,¹²⁵ which enhance the receptor function. Secondly, the single crystalline core provides quick transport to the charge carriers that take place during the interaction of gas molecules with the nanowire, which enhances transducer functions. Sensing properties of these nanowires with and without ZnO shell have been investigated on both oxidizing and reducing class of gases.

5.1.2 Experimental details

In₂O₃-ZnO core-shell nanowires were grown in a CVD double tube VLS furnace in a two-step growth process (as discussed in chapter 3). In the first step, core In₂O₃ nanowires were synthesized at 900°C source temperature using 9 nm gold layer as catalyst for the nanowire growth on alumina substrate with growth duration of 30 min. In the second step, smaller growth duration of 5 min was used for the growth of the ZnO shell on the In₂O₃ core without catalyst. The source temperature and the argon flow rate were kept constant at 900°C and 50 sccm respectively, as in the first step. Final products on the alumina substrate were formed near the lower temperature end (450-500°C) of the quartz tube.

The resistor based sensing devices were fabricated by using a platinum interdigitated electrode pattern deposited by sputtering over the pristine In₂O₃ and In₂O₃-ZnO core-shell nanowires and a Pt coil at the backside of the alumina 2x2 mm² substrate was deposited for precise heating. The distance between the interdigitated contacts was 200 µm. The sensor devices were operated by applying a constant voltage to the Pt heater at the back of the substrate and the same Pt resistance coil was also used as a thermometer to measure the temperature precisely. The selection of substrate for the sensor platform plays an important role especially in higher temperature operations. Higher working temperature can produce leakage through the substrate which deteriorates the sensor response. So it is useful to use a poor electronic conducting substrate with high thermal conductivity (e.g. alumina) for the high working temperature resistor based devices.

The responses of the core-shell nanowires to different gases were measured by monitoring the resistance/conductance of the device. A constant synthetic air flux (0.3 l/min) at atmospheric pressure was used as gas carrier for the dispersion of the analyte gases in the

desired concentration. All sensing related measurements were performed in a sealed sensing chamber (volume ~1L) under 50% RH. The conductance of the sensor device was monitored by the volt-amperometric method at a constant voltage bias of 1 V. The sensing properties were characterized at working temperatures between 100 and 400 °C. All the sensor devices were pre-stabilized at the working temperature for 10 h, before any sensing measurements. Different concentrations of all sensing gases were achieved by diluting a known concentration of gas in air. The sensor response (S) was defined as the “ratio of the device resistance (conductance) in oxidizing (reducing) gas to that in air” respectively.

5.1.3 Result and Discussion

The typical morphology of In_2O_3 nanowires is shown in Figure 5.1(a) which is serving as core in the hetero-structure. The nanowires were found to be single crystalline with an average diameter of ~150 nm and a length of 5-20 μm on the alumina substrate. On these nanowires, ZnO shell layer was grown without using any catalyst for a short deposition time of 5 min to maintain a low thickness (15-25 nm). The resultant core-shell nanowires are shown in Figure 5.1(b), with a grainy particle-like ZnO shell layer decorating the nanowire core (in the inset of the Figure 5.1b).

Figure 5.1 FESEM images of; (a) as grown In_2O_3 nanowire serving as core, (b) after deposition of the ZnO shell layer and inset shows the magnified view of the hetero-structure surface, (c) device, (d) the area selected in red square in Figure 5.1c. Figure 5.1(e) shows the wide area EDX pattern obtained from the as grown core-shell nanowire sample.

These granules on the surface were found to be polycrystalline ZnO which will be discussed later in this section. Figure 5.1(c and d) shows the SEM image of the device and nanostructures at the channel of the device, respectively. The presence of Zn, In and O was confirmed by the broad area EDS study on the as grown samples (Figure 5.1e) where sharp peaks of Zn (L-line), In (L-series) and O (K-line) were obtained. Detailed study of the crystal structure and composition of the single core-shell nanowire was performed under TEM. Figure 5.2(a) shows the TEM image of a typical In_2O_3 -ZnO core-shell nanowire with the granular ZnO on the surface. HRTEM image (Figure 5.2b) of the single core-shell nanowire shows the single crystalline core (cubic indium oxide) and poly crystalline ZnO shell, which was confirmed by the SAED patterns obtained from the core and shell regions as shown in Figure 5.2(c and d). SAED patterns were indexed for single crystalline cubic phase of In_2O_3 along zone axis (ZA) [102] and polycrystalline rings were obtained for the wurtzite ZnO. In

polycrystalline phase, different planes form ring patterns in the diffraction space. Thus, the ring patterns demonstrate that the ZnO shell is polycrystalline. The rings; A, B, C and D correspond to the reflection from wurtzite ZnO planes of (100), (002), (102) and (110) respectively. More investigations on the composition of core-shell nanowires were done by a TEM-EDS study on a single nanowire. TEM-EDS elemental line profiles for zinc, oxygen and indium are shown in Figure 5.2(e). These line profiles were obtained along a line which was drawn perpendicular to the diameter of the In_2O_3 -ZnO core-shell nanowire (inset of Figure 5.2e). The intense Zn peaks at the two ends indicate the presence of Zn shell layer in the hetero structure. On the other hand, In is located in the middle of the nanowire. These line profiles indicate the formation of In_2O_3 -ZnO core-shell nanowires.

Figure 5.2 TEM analysis of (a) as grown hetero-structure showing the grainy outer surface, (b) HETEM image of the same, (c) SAED pattern obtained from the outer shell shows the polycrystalline diffraction rings of wurtzite ZnO, (d) SAED pattern obtained from the core area of the hetero structure, shows the diffraction pattern of a single crystalline cubic phase

of the In_2O_3 and (e) demonstrates the TEM-EDS study, a line profile obtained from a single nanowire (shown in the inset).

Typically, VLS (for core In_2O_3) and VS (for ZnO shell) condensation can lead to formation of core-shell structures. The VLS growth mechanism is discussed in chapter 4, for the core In_2O_3 nanowires, where gold is serving as a catalyst in the nanowire growth in a small quartz tube. ZnO shell was deposited without using any catalyst; as a result random nucleation of ZnO takes place on the In_2O_3 nanowire surface which leads to the formation of granular structures. Due to the smaller deposition duration and low synthesis temperature, the formation of polycrystalline ZnO shell takes place. The unique structure possesses certain advantages when used as a chemical sensor. The grainy and rough outer surface of the nanostructure creates more adsorption sites (due to higher defects) for the gas molecule.¹²⁵ There are homo and hetero nano-junctions present in the multiple nanowire samples which create different potential barriers on the percolation paths of the electron. Modulation of these potential barriers and higher gas adsorption on the grainy surface can enhance the sensor response. ZnO has been previously used as a shell on SnO_2 , TiO_2 and Fe_2O_3 in a core-shell structure to enhance the gas sensing properties.^{118, 121, 124} Because of the different growth methods/conditions, single crystalline ZnO shell was obtained in these works.^{118, 121,}¹²⁴ Lao et al.¹²⁶ have reported the formation of In_2O_3 -ZnO hetero-structures with In_2O_3 core and ZnO secondary arms. It has been observed that one step growth of the hierarchical (In_2O_3 core and ZnO secondary arms) forms single crystalline nanostructures.

The potential applications of the pristine In_2O_3 and core-shell In_2O_3 -ZnO nanowires as a chemical sensor were tested. Their sensing properties toward oxidizing and reducing

gases were investigated in various concentrations under different working temperature. Both types of nanowires were tested for CO (50-400 ppm) NO₂ (0.2-1 ppm), Ethanol (100 ppm – 400 ppm) and Hydrogen (1000-4000 ppm) at different working temperature (100°C - 400°C).

Figure 5.3 A representative plot of dynamic sensor responses obtained from the devices based on, (a) pristine In_2O_3 nanowires and (b) In_2O_3 -ZnO core-shell nanowires.

The gas flow rate was kept constant at 300 sccm during the whole experiment for all gases. Figure 5.3 shows the typical sensor response plot for both types of nanowires towards different concentrations of ethanol vapors. First two cycles were measured with the same concentration to avoid any false response in first exposure. Figure 5.4 summaries the sensor responses for various gases with different working temperature and Figure 5.5 depicts the comparison of all gases tested for both types of devices. A maximum sensor response for CO, H₂ and NO₂ was obtained in the temperature range of 300-350°C whereas for ethanol the maximum sensor response was found near 350-400°C for both devices. The respective response time of In_2O_3 and In_2O_3 -ZnO hetero-structures nanowires (measured at their

respective optimum sensor response) are; 9 min and 4.4 min for 100 ppm ethanol, 7 min and 10.6 min for 200 ppb NO₂, 2 min (unstable response) and 6 min for 1000 ppm H₂.

It can be observed that the ZnO-In₂O₃ nanowires sensor shows higher response toward CO, ethanol and hydrogen gases (which are reducing species) compared to the oxidizing gas NO₂ (Figure 5.5). The NO₂ concentrations used in the experiment were relatively low compared to the other two gases, because of its highly oxidizing nature. Pristine In₂O₃ nanowires show significantly better response (maximum at 350°C working temperature) towards NO₂ which is almost 5.5 times higher than In₂O₃-ZnO core-shell nanowires (for 1 ppm NO₂). The resistance of pristine In₂O₃ nanowires responds well to the environment of NO₂ gas when the working temperature is higher than 200°C. The resistance of the sensor device rises very quickly at the introduction of NO₂ gas at even 0.2 ppm. and the resistance decreases as soon as the gas exposure stops. A high sensor response of ~5.4 ($\pm 9.3\%$) from low concentration of 200 ppb NO₂ for pristine In₂O₃ nanowires was obtained (Appendix, supporting information S1). In contrast, core-shell nanowires showed a lower sensor response ($\sim 1.45 \pm 11.2\%$) with longer response time for the same gas concentration. In literature, pristine In₂O₃ nanowires have been found very sensitive and selective towards NO₂ gas.^{127, 128} Rout *et al.*¹²⁷ have reported high sensor response of ~44 for 1 ppm NO₂ at 150°C from In₂O₃ nanowires (20 nm diameter) prepared by template assisted growth. Xu *et al.*¹²⁸ have reported a sensor response of ~2.5 for 1 ppm NO₂ at 250°C from In₂O₃ nanowires in comparison to a sensor response of ~17.5 for 1 ppm NO₂ at 350°C from In₂O₃ nanowires in this work. Other metal oxide nanomaterials such as ZnO nanorods (1.4 at 100 ppb NO₂),¹²⁹ SnO₂ nanobelts (2.3 at 300 ppb NO₂),¹³⁰ and WO₃ nanowires (21 at 10 ppm NO₂)¹²⁷ were also found to be attractive towards NO₂ detection.

For reducing gases, the responses of the devices show opposite behavior for the oxidizing gas (NO_2). As evident in Figure 5.4 and Figure 5.5, the In_2O_3 -ZnO core-shell nanowires show enhanced sensor response for reducing gases compared to the pristine In_2O_3 nanowires show enhanced sensor response for reducing gases compared to the pristine In_2O_3 nanowire sensor. A sensor response of ~ 7 ($\pm 3.1\%$) for 2000 ppm H_2 was obtained from core-shell nanowires in comparison to ~ 2 ($\pm 6.5\%$) of the pristine In_2O_3 for the same concentration of H_2 .

Figure 5.4 Gas sensing profiles of (a) In_2O_3 and (b) In_2O_3 -ZnO core-shell nanowire devices toward CO (100 ppm), NO_2 (1 ppm), H_2 (2000 ppm) and ethanol (100 ppm).

A high sensor response of ~ 265 ($\pm 7.1\%$) for 400 ppm ethanol at 350°C was obtained from In_2O_3 -ZnO nanowire compared to the maximum sensor response of ~ 17 ($\pm 4.5\%$) from the In_2O_3 nanowire at 400°C for similar gas concentration (Figure 5.5). This result shows the high selectivity of the In_2O_3 -ZnO nanowire for ethanol. The dynamic repeatability was

observed for different gases in the same experiment by exposing gases one after another for more than 26 hrs. The sensor device was found repeatable and stable for all gases.

5.1.3.1 Sensing Mechanism

In the network based nanowire chemical sensors, large inter nanowire junctions formed along the percolation path of charge carriers. In the pristine In_2O_3 nanowire sensor only homo junctions formed along the channel. In contrast, combinations of homo- and hetero junctions formed in the In_2O_3 -ZnO core-shell nanowire sensor. A significant difference in the sensor response was noticed for reducing and oxidizing gases when compare these two types of nanowires. A significantly higher response for H_2 and ethanol was obtained from In_2O_3 -ZnO nanowires in comparison to pristine In_2O_3 while for pristine In_2O_3 nanowires showed a better response for NO_2 (Figure 5.5). The presence of ZnO shell layer creates hetero junctions (In_2O_3 -ZnO) which provides additional energy barrier at the junction, augmenting the change in resistance of the nanowires towards gas exposure. In the sensing mechanism of these devices, the role of polycrystalline shell layer and junctions between the core-shell nanowires need to be considered.

Figure 5.5 The gas sensing performances of In₂O₃ and ZnO-In₂O₃ core-shell nanowires with their respective optimized working temperatures are plotted with the same gas concentration for both types of nanowires: H₂ (4000 ppm) @ 300°C & 350°C, NO₂ (1 ppm) @ 350°C & 300°C, CO (400 ppm) @ 350°C & 400°C and ethanol (400 ppm) @ 400°C & 350°C for In₂O₃ and ZnO-In₂O₃ respectively.

In the pristine In₂O₃ nanowires at high working temperature of 100–400°C, a depletion layer exists at the surface due to oxygen chemisorption. Thus the chemisorptions of oxygen ions increase the nanowire resistance by reducing the active nanowire channel volume. Upon gas exposure, the nanowire surfaces change its resistance/conductance depending on the oxidative or reductive interaction between nanowire material and gases. Along with the variation in resistance of the nanowire during sensing, contacts between nanowires determine the final response of the sensor device.

In the In_2O_3 -ZnO core-shell nanowire, an electron depletion layer forms at the interface due to the differences in work function of the core and shell materials, responsible for the electron transport in the nanowire core. The relative work functions of the metal oxides depend on the degree of non-stoichiometry.¹³¹ Chemisorption of the oxygen from ambient onto the surface of the ZnO shell layer creates an additional electron depletion layer at the core-shell interface (refer to Figure 5.6b). The thickness of this depletion layer plays a crucial role in the carrier transport between sensing gas and nanowire material¹⁰⁷. In the metal oxides, the depletion layer thickness exists in a range of 11-21 nm for a working temperature of 327 – 427°C.¹³² A thin shell layer may get fully depleted resulting in complex effect on the sensing mechanism¹⁰⁷. Upon exposure to oxidizing gases, the initial depletion layer (before exposure) in the ZnO shell further extends and connects with the interface (between In_2O_3 -ZnO) depletion layer. As a result, the resistance of the device increases due to the formation of the large depletion region. In such conditions, in order to further change the sensor response, adsorbed gas molecules withdraw electrons from the core of the nanowire which needs a larger energy to cross the large depletion region. As a result, the core-shell nanowire sensor response decreases for NO_2 gas (from 16 of In_2O_3 to 3 for 1 ppm NO_2 , shown in Figure 5.4a and b). In the literature, *Hwang et al.*¹⁰⁷ have observed a slight increase in the NO_2 sensor response (from 1.6 to 2.3 for 10 ppm NO_2) for ZnO- SnO_2 core-shell (with single crystalline SnO_2 shell) nanowire sensor which is small compared to the increase in the reducing gases sensor response (41 to 280 for 200 ppm ethanol, 2.5 to 8.3 for 200 ppm H_2). In our findings on the selectivity for the reducing gases, polycrystalline ZnO plays a crucial role. When the shell layer is polycrystalline, the grain boundaries create additional energy barriers which alter the ease of electron transport. In contrast, electron

depletion layer thickness at the surface reduces upon exposure of reducing gases (due to injection of electrons from reducing gas species into the nanowire), as a result reducing gases (e.g. H_2 , ethanol) show high response to the core-shell structure.

Figure 5.6 Illustration of the charge transport through (a) homo-structures nanowire junction followed by cross section contact and formation of an energy barrier at the junction, (b) hetero-structured core-shell nanowire junction followed by the cross sectional view with two depletion regions and formation of three energy barriers at the interfaces.

A grainy polycrystalline surface possesses higher energy due to the presence of surface terminated dangling bonds making them favorable for the adsorption of gas molecules.¹²⁵ The presence of the polycrystalline shell layer and its grain size plays a crucial role in defining the selectivity for oxidizing and reducing gases.^{133, 134} The larger grain size of ZnO shell layer in the core-shell nanowire is the main factor of its poor responses for

oxidizing gases. This was corroborated by the findings on the thin film based sensors,^{133, 134} where it was observed that oxidizing gases were very sensitive to the grain size effects with diminished and muted sensing responses at larger crystal size (80-100 nm).

Percolation paths of the electrons in the nanowires network are composed of multiple nano-junctions with a potential barrier at each junction. The height of the potential barrier at the homo junctions mainly depends on the surface states, oxygen vacancies and the depletion layer on the nanowire surface due to chemisorptions of oxygen ions.^{135, 136} The potential barrier in the hetero junctions is more complex and depends on the work function and band gap differences between the two materials forming hetero-structure, as well as the presence of eventual surface states¹³⁷. Because of the complexity of properly determining surface states, the band structure is often approximated ignoring their effects and the Anderson's model is being applied.¹³⁸ In this frame, the barrier at the ZnO-In₂O₃ interface is asymmetric, with a depletion layer building up in the ZnO side and an accumulation layer building up in the In₂O₃ side. A schematic diagram is shown in Figure 5.6.

At an inter nanowire junction (between two In₂O₃-ZnO core-shell nanowire), there are three energy barriers involved (shown in Figure 5.6b); two barriers at the hetero-interfaces between In₂O₃-ZnO in each core shell nanowire and one at the homo-interface between the polycrystalline ZnO shells of two nanowires. At the junction of the two core-shell nanowires, charge carriers have to percolate through all three potential barriers (which are connected in series) in order to reach to the other nanowire. The exposure of oxidizing gases (NO₂) to such device further increases the potential barrier height by withdrawing electrons from the nanowire; as a result less charge carriers cross the barrier (under a constant applied bias) and the device conductance decreases. The relative change in the current before

and after exposure to NO_2 is small due to the initial large potential barrier height which reflects as low response to the oxidizing gases. On the other hand, exposure to reducing gases (such as H_2 and ethanol) lowers the potential barrier height due to their electron donating nature which allows more charge carriers to pass through the barrier, resulting in a higher response towards the reducing species. Thus, the combined effect of the polycrystalline ZnO shell layer and modulation of potential barriers on the percolation path upon gas exposure, defines the sensor behavior for different gases. The significant enhancements in the sensor response and selectivity for the reducing gases have been achieved by the presence of polycrystalline ZnO shell on In_2O_3 nanowire core.

5.1.4 Summary

The role of polycrystalline ZnO shell layer in a core-shell nanowire has been investigated in the sensing of different class of gases. Grainy outer shell layer was observed to increase the adsorption of gaseous species which play a vital role in the enhanced sensor response for pollutant gases. The formation of multiple junctions (both homo- and hetero-) in the core-shell nanowires based sensors is the main reason for the improved sensor response toward reducing gases in comparison with the pristine In_2O_3 nanowires. However, pristine In_2O_3 nanowires were observed to be shown a better response towards NO_2 (oxidizing gas).

5.2 Zn-doped In₂O₃ nanowires network based resistor devices for gas sensing

5.2.1 Introduction

Conductometric gas sensors based on 1D MOx (e.g. SnO₂, In₂O₃, ZnO etc.) have been the subject of extensive investigations because of their high sensitivity to oxidizing and reducing gases.¹³⁹⁻¹⁴² Majority of the MOx are n-type semiconductors. The oxidizing and reducing gases induce a resistance/conductance change on the n-type semiconductor. The explanation for resistance/conductance change during sensing is related to the transfer of electrons between the semiconducting nanowire and adsorbed gas molecules.¹⁴³⁻¹⁴⁵

Several technological progresses have been made to enhance the sensor response. The utilization of different dopants and metal nanoparticles decoration has been explored.^{146, 86, 147, 148} The sensitivity and selectivity of In₂O₃ based chemical sensors to different gaseous species have been changed by the doping of different metal ions.^{149, 150, 142, 151} Undoped In₂O₃ nanowires have been found to be very sensitive to NO₂ gas.^{152, 153} Ppb level detection of NO₂ has been reported at room temperature using single and network In₂O₃ NW devices.¹⁵³ Doping serves to alter the carrier concentration in the nanowire and hence the position of Fermi level in the semiconductor band gap. *Zhang et al.*¹⁵¹ have reported a contrasting sensor response for NH₃ gas for a low and high doping of oxygen vacancies in In₂O₃ nanowires.

5.2.2 Experimental Methods

Zn-In₂O₃ nanowires were synthesized in a horizontal double tube VLS (vapor-liquid-solid) furnace as described in previous chapters. In brief, a mixture of ZnO and In₂O₃ powders with graphite powder was heated at 900°C source temperature using 9 nm gold layer as catalyst for the nanowire growth on alumina substrate with growth duration of 30 minutes. During the deposition, argon gas flow rate was fixed at 50 sccm and the pressure inside the quartz tube was maintained at 1 mbar.

The sensor fabrication method and gas sensing procedures were similar to the In₂O₃-ZnO core-shell nanowires as discussed in section 5.1.2. Both undoped and Zn-doped In₂O₃ nanowires based devices were tested to CO (100-400 ppm), NO₂ (0.2-1 ppm), ethanol (50-400 ppm), hydrogen (1000-4000 ppm) and acetone (20-100 ppm) at 100 - 400°C working temperatures. The gas flow rate was kept constant at 300 sccm during the whole experiment for all gases while humidity was kept constant at RH=50% @ 20°C. The effect of relative humidity (RH) from 0 % (dry air) to 70 % was measured for NO₂ gas on both types of devices at the optimum working temperature of the individual device.

5.2.3 Result and Discussion

The morphology of the as synthesized nanostructures is shown in the FESEM images in Figure 5.7(a and b). Nanowires diameter ranges from 70 nm to 150 nm with a length of few tens of micro-meters (Figure 5.7b). The variation in the diameter could be due to the variation in the Au catalytic particle sizes which generally controls the diameter in a VLS growth. The TEM analysis on single Zn-In₂O₃ nanowire is shown in Figure 5.7. SAED pattern was collected along [102] zone axis (ZA) in a cubic indium oxide crystal system and

has been identified accordingly (Figure 5.7c). Low magnification TEM image in Figure 5.7d confirms the VLS growth of the nanowires where it can be seen that Au is present on the top of the nanowire. Figure 5.7e shows the HRTEM image with atomic planes indicating the high crystalline quality of the Zn-In₂O₃ nanowires. The measured interplanar distance of ~ 0.57 nm corresponds to (111) interplanar distance. The Zn doping characterizations can be found in chapter 6 where 1.6 at. % of Zn insertion in to In₂O₃ lattice was found.

Figure 5.7. Microscopic analysis of the Zn-In₂O₃ nanowires; (a) and (b) show the high and low magnification FESEM images respectively, (c) SAED pattern measured along [1,0,2] zone axis and patterned accordingly, (d) low magnification TEM image of single Zn-In₂O₃ NW with Au at the tip indicates VLS growth and (e) HRTEM image of the Zn-In₂O₃ nanowire with an interplanar distance of ~ 0.57 nm which is corresponding to (111) interplanar distance.

The application of the In_2O_3 and $\text{Zn-In}_2\text{O}_3$ nanowires as a conductometric chemical sensor was investigated for different gases in various concentrations at different working temperatures. Figure 5.8 shows the typical sensor response plot for both types of nanowires toward different concentrations of all gases at a working temperature of 350°C . Figure 5.9(a and b) summarizes the sensor responses for various gases with different working temperature and Figure 5.9c depicts the comparison of all gases tested for both types of devices. Comparing both devices, a higher sensor response for CO, H_2 , ethanol and acetone (reducing gases) from $\text{Zn-In}_2\text{O}_3$ NW and for NO_2 from In_2O_3 was obtained (Figure 5.9c). Optimum sensor responses for pristine In_2O_3 NW were observed in the temperature range of $300\text{--}350^\circ\text{C}$ whereas for $\text{Zn-In}_2\text{O}_3$ NW, the maximum sensor responses were found in the temperature range $350\text{--}400^\circ\text{C}$ for all gases.

Figure 5.8 Responses of In_2O_3 and $\text{Zn-In}_2\text{O}_3$ nanowires devices for different gases at 350°C working temperature.

Pristine In_2O_3 nanowires show a high sensor response of ~ 17.5 (maximum at 350°C working temperature) for 1 ppm NO_2 . In contrast, $\text{Zn-In}_2\text{O}_3$ nanowires show a reduced sensor response of ~ 6.5 for 1 ppm NO_2 at 200°C . Unusual sensor responses at higher operating temperatures (300°C and above) from $\text{Zn-In}_2\text{O}_3$ nanowires towards NO_2 were observed (Figure 5.8 and Figure 5.9c). Instead of reduction in the conductance, $\text{Zn-In}_2\text{O}_3$ nanowire showed an increase in the conductance while exposing NO_2 at higher working temperature. This behavior may be due to a consequence of n-p semiconductor transition. As a native n-type semiconductor, there are always oxygen related vacancies present in In_2O_3 . Zn-doping can increase the oxygen vacancies and surface defects significantly.^{154, 155} Higher defects present in the nanowire adsorb more oxygen species from the surroundings.¹⁵⁶ At higher operating temperature, adsorbed oxygen species on the surface of the $\text{Zn-In}_2\text{O}_3$ nanowire diffuse into the bulk of the nanowire and incorporate into the oxygen vacancies.^{157, 158} The incorporation of the oxygen atom into the vacancies can be understood by the following reaction;

where $\text{V}_\text{o}^{\bullet\bullet}$ represents oxygen vacancies and O° represents oxygen atom in an oxygen site.¹⁵⁹ Reaction (i) happens at higher working temperature (above 300°C). The above reaction reduces the electron concentration because of the incorporation of oxygen atoms into oxygen vacancies and NO_2 adsorption on the nanowire surface. Due to the decrease in electron concentration, a down shift in the Fermi level in $\text{Zn-In}_2\text{O}_3$ nanowires is expected. In addition, Zn-doping also contributes to the downward shift in the Fermi level when Zn^{2+} replaces In^{3+} in the cubic In_2O_3 system. The down shift in Fermi level can cause the transfer of electrons

in opposite direction,¹⁵¹ which results in opposite sensor response. Similar unusual sensing behavior towards NO₂ from ZnO nanotubes have been observed by Wang *et al.* when operating temperature switched from low (50°C) to high (100°C and above).¹⁶⁰ The opposite sensing response has been attributed to the unusual p-n transition at low temperature and low concentration.

Figure 5.9 Sensor responses of, (a) Zn-In₂O₃ nanowires and (b) In₂O₃ nanowire for different gases at different working temperature and (c) shows the sensor response comparison of both the devices for H₂ (4000 ppm), CO (400 ppm), NO₂ (1 ppm), ethanol (100 ppm) and acetone (100 ppm) at the optimized working temperature of the respective devices

On the other hand, Zn-In₂O₃ nanowires were observed to significantly enhance the sensor responses for CO, H₂ and ethanol. High sensor responses of ~21.5, 32.5 and 60 were obtained from Zn-In₂O₃ nanowires for 400 ppm CO, 4000 ppm H₂ and 100 ppm ethanol respectively. In contrast, In₂O₃ nanowires show lower sensor responses of 4.7, 4.5 and 3 for the same gas concentrations of CO, H₂ and ethanol gases respectively (Figure 5.9). The significant enhancement in the sensor response of CO, H₂ and ethanol can be attributed to the Zn- insertion into the In₂O₃ lattice. Higher oxygen vacancies and surface defects present in Zn-In₂O₃ nanowires enhance the adsorption of gaseous species on the surface.¹⁵⁶ To maintain the charge balance, the doping of Zn²⁺ generates excess lattice oxygen-ion vacancies which have two distinct effects. Firstly, it improves the sensor receptor function by enhanced surface oxygen chemisorption (O²⁻ and O⁻ ions), and secondly it improves the transducer function of the sensor by the increased space-charge layer thickness.¹⁶¹

Figure 5.10 Calibration curves for NO_2 gas at different relative humidity (0 – 70 %) at 350°C using; (a) In_2O_3 and (b) $\text{Zn-In}_2\text{O}_3$ nanowires sensor. Figure (c) and (d) summaries the “z” values for In_2O_3 and $\text{Zn-In}_2\text{O}_3$ nanowires respectively, corresponding to different relative humidity.

In the nanowire network sensors, there are large numbers of inter-nanowire junctions present along the conducting path. At each junction, a potential barrier exists and controls the resistance of the path. During reducing gases exposure, the chemisorbed oxygen species are consumed which return the electrons to nanowire, leading to lower the overall channel resistance.^{162, 163} In contrast, upon exposure of NO_2 (oxidizing gas), target gas and oxygen adsorb (on the nanowire surface) competitively as anions on the nanowire surface. As NO_2 gas is known to adsorb as an anion (NO_2^-), which competes with the pre-adsorbed oxygen

species. In order to change the device resistance during NO₂ exposure, NO₂ molecules compete with chemisorbed oxygen.¹⁶³ The overall reactions for both types of gases can be understood as follows;

-where R in (iii) represents the reducing gases (e.g. CO, H₂ etc).

The power law model ($S = A * C^z$ where S is sensor response, A is a constant and C denotes the concentration of the target gas) has been used to calculate the value of exponent z.^{150, 164, 163} According to this model, if the value of z is closer to 0.5, the adsorption of gas is dissociative dominated and if the value of z is closer to 1, the adsorption is mainly non-dissociative. Figure 5.10 shows the calibration curves for the NO₂ gas for both devices at different RH values which relate the changes in sensor response for various concentrations of NO₂. All the values of z for In₂O₃ and Zn-In₂O₃ with different RH values have been summarised in the tables of Figure 5.10. The value of z for In₂O₃ nanowires ranges from 0.73 to 0.87 for the corresponding RH values from 0 to 70%. So far, the NO₂ sensing mechanism appears having mixed behaviour of dissociative and non-dissociative adsorption, but at high humidity values (RH=70%), a value z=0.87 suggests a dominance of non-dissociative adsorption phenomena.^{150, 164, 163} On the other hand, Zn-In₂O₃ nanowires show a decrease in the z value from 1.18 to 0.62 for the corresponding increase in the RH values of 0 to 70%. The decrease in the z values with an increase in the RH values indicates the shifting of dominance in NO₂ adsorption from non-dissociative to dissociative on Zn-In₂O₃ nanowires surfaces. The dissociative NO₂ interaction with Zn-In₂O₃ at higher RH values (more than

50%) leads to the formation of atomic oxygen species on the surface. It is postulated that the atomic oxygen species incorporate into the vacant oxygen sites in Zn-In₂O₃ nanowire at higher working temperature (300-400°C), which results in an opposite sensor response discussed earlier.

Selective response to NO₂ from pristine In₂O₃ nanowires was observed over CO, H₂ and ethanol gases, in agreement with past findings on FETs where In₂O₃ nanowires have been found to be very selective towards NO₂.^{152, 153} In comparison, Zn-In₂O₃ nanowires have shown larger sensor response for ethanol, H₂ and CO over NO₂ when tested under similar working conditions. After Zn- doping into In₂O₃, sensor response towards NO₂ reduces significantly and an opposite sensor response was observed towards higher temperature. In contrast, Zn- doping enhanced the sensor response for ethanol, H₂ and CO gases which pave a way to the selective detection of reducing gases over oxidizing gases (e.g. NO₂).

5.2.4 Summary

Zn- doping into the In₂O₃ nanowires have enhanced the sensor response for H₂, ethanol and CO (reducing gases) while pristine In₂O₃ nanowires have shown better response for NO₂ (oxidizing gas). Zn-In₂O₃ nanowires have shown ~5, 7 and 15 times enhanced sensor response for 400 ppm CO, 4000 ppm H₂ and 400 ppm ethanol respectively compared to pristine In₂O₃ nanowires. Zn incorporation into the In₂O₃ lattice creates more oxygen vacancies and increases the surface defects which enhance the receptor function for reducing gases. NO₂ calibration curves on Zn-In₂O₃ nanowires at different RH indicate that the interactions of NO₂ molecules are dissociative towards higher relative humidity.

Chapter 6

Chemical sensors based on single NW-FET device

In this chapter, the chemical sensing properties of single nanowire based field effect transistor (NW-FET) devices have been explored. This chapter mainly consists two major sections; first section is mainly dedicated to elucidate the effect of contacts between semiconducting nanowire and metal electrodes on chemical sensing. The second section deals with the nanowire channel effect on the sensing performance of NW-FET.

6.1 Effect of the contacts on NW-FET sensor response

In this section, the investigation on the role of contacts between semiconducting nanowire and metal electrodes in a single nanowire FET on the sensing of different type of gases is presented. Two different types of In_2O_3 nanowire devices, namely; Schottky contact device (SCD) and Ohmic contact device (OCD) are evaluated. SCD has shown a superior response to the reducing gas (CO) compared to oxidizing gas (NO), while OCD has shown high sensitivity towards oxidizing gas (NO) compared to the reducing gas (CO) under similar working conditions. The sensing mechanism is dominated by the contact resistance at metal-semiconductor junction in SCD and the change in nanowire channel conductance dominates in OCD. Schottky barrier height (SBH) is extracted using low temperature current voltage measurement which provides direct evidence for the notion that the barrier height is playing a

crucial role in sensing of the different types of gases. The sensing mechanism is illustrated for both devices.

6.1.1 Introduction

MOx semiconducting nanowire systems are one of the most promising material systems for the application in chemical sensing. These 1-D nanostructures possess advantages such as large surface-to-volume ratio, higher crystallinity and better stoichiometric control.¹⁶⁵⁻¹⁶⁷ The conductometric chemical sensors function by producing observable conductance variations from surface catalytic chemical processes. Nanocrystalline In₂O₃ based chemical sensors are promising candidates for the sensing of toxic gases in environmental monitoring such as NO₂, CO, NH₃ etc.^{168, 153} In₂O₃ based sensors have been found attractive for the selective sensing of CO gas.¹⁶⁹ The near-surface region in In₂O₃ nanowires becomes depleted of electrons due to the chemisorbed oxygen species.¹⁶⁵ During reducing gas (e.g. CO) exposure an interaction of gas molecules to chemisorbed oxygen species leads to electron transfer back into the nanowire, thereby increasing the conductivity.¹⁶⁵ Adsorption and desorption of gas molecules on metal oxides are both thermally activated processes, which cause the response and recovery times to be usually slow at room temperature. Development of room-temperature gas sensors has very important advantages such as low power consumption, simple system configuration, reduced explosion hazards and longer device lifetime. Quasi 1D MOx semiconducting nanostructures have shown promising results¹⁷⁰⁻¹⁷² mainly due to their desirable large surface to volume ratio, single crystalline nature, ease of fabrication on various substrates by different techniques^{173, 174}. Single NW-FET based conductometric sensors have shown the capability of room temperature

operation¹⁷⁵⁻¹⁷⁹. In such devices, gas molecules directly interact on the single crystalline nanowire surface (with a small cross sectional area) with simple device geometry which alters their electronic properties and reflects as a change in the conductance of the device.

Most of the past efforts on nanosensors have been focused on improving the sensitivity by modifying the nanowire channel; mainly by surface modification using polymer or metal nanoparticle functionalization to the nanowire channel,¹⁷⁶⁻¹⁷⁸ doping of nanowire etc.¹⁸⁰ Recently there are some reports on the utilization of the contact resistance at the nanowire-electrode interface to improve the sensitivity.^{181, 182, 85, 183, 184}

In a conductometric sensor, the sensor response is the relative change in the conductance before and after detection species exposure. There are mainly two components in a single nanowire sensor which directly contribute to the sensor response; the nanowire channel and contact resistance between electrode and nanowire [metal–semiconductor (MS) contact]. These contacts may be either Ohmic or Schottky type, and both types of contact are important in sensing. In a single nanowire FET based sensor, the devices are mainly fabricated for Ohmic contacts to improve the sensor performance. However, it may not always be advantageous to have an Ohmic contact. Schottky contact devices are interspersely reported to be a highly sensitive device for gas sensing.^{181, 182, 85, 184} The contact resistance contribution towards sensor response may vary significantly for different type of gases; as a result SBH modulation takes place during sensing due to the gas molecule interaction at the MS interface which plays an important role in the sensor response. Wei et al.⁸⁵ have reported a four orders magnitude higher in sensor response for 400 ppm CO gas at 275°C by using one end Schottky contact device made of ZnO nanowire operated in reverse biased mode in comparison to an Ohmic device operated at similar conditions. The gas sensing mechanism

of such devices is mainly dominated by the SBH modulation through surface reactions at the MS interface.

The goal to realize sensors at room temperature with a high response remains unfulfilled with critical challenges. Past research efforts on contact resistance utilization for the gas sensing did not reveal any clear trend in the sensing behavior toward two different classes of gases (e.g. oxidizing and reducing). A systematic study is required to investigate the sensing behavior of both Schottky and Ohmic devices toward oxidizing and reducing gases. This work provides insight on the contact junction modulation to achieve improved sensor response at room temperature and selectivity for a particular class of gas. We have used two different types of devices (OCD and SCD) for the sensing of two different classes of gases [namely; CO (reducing gas) and NO (oxidizing gas)] by differentiating control of the contact resistance of the device to improve the sensor response at room temperature. In SCD we have used Schottky contact at both ends of the nanowire which gives the advantage to operate the device in both reverse and forward bias mode. In OCD, the nanowire channel plays a dominate role. The results presented here show a step forward in the understanding on the utilization of the contact resistance in room temperature gas sensing of different class of gases and set the path for the smart future sensor devices at room temperature.

6.1.1.1 Semiconductor surfaces and Metal-Semiconductor (MS) interface

The electronic properties of a semiconductor are much influenced by its surface. There are large numbers of unsatisfied dangling bonds present at the surface which makes the surface at high energy state. As a result, surfaces tend to re-construct to minimize its surface energy, and return to overall charge neutrality. There are surface states present inherently in a

semiconductor which dominate the characteristic of the semiconductor surface. These surface states distributed within the energy band-gap of the semiconductor which can be either acceptor or donor type. If the density of donor type states is larger, the surface state lies closer to the conduction band minima (CBM). Similarly if the acceptor states density is larger, the surface state lies close to the valence band maxima (VBM). At a certain energy location within the band gap the acceptor state density matches the donor state density and the cross-over point is known as the charge neutrality level (CNL). CNL has special significance in the physics of hetero junctions and interfaces. The intrinsic band bending is determined by the relative difference between CNL and the equilibrium Fermi-energy (E_F) level. When E_F is above the CNL, positive charge is stored in the surface states, and for an n-type semiconductor a slightly downward band bending results.

Figure 6.1 Band bending and surface dipole under (a) surface depletion and (b) accumulation conditions.

On the contrary, when the CNL is above E_F , a net negative charge appears in the surface states. As a result, the bands bend upwards resulting in a surface depleted condition. Figure

6.1 shows the two different conditions discussed above. A surface dipole layer forms between the charge stored in the surface states (Q_{ss}) and the charge induced in the semiconductor (Q_{sc}). At band condition arises when the CNL coincides with the Fermi-level position, but in most semiconductors, the CNL differs from the Fermi level by a few tenths of an eV giving rise to either surface depleted or accumulated conditions. The semiconductor band structure, growth and surface preparation conditions decide the magnitude and direction of the surface dipole. Apart from the above mentioned facts, the semiconductor surface properties are also influenced by the introduction of a metal layer on the semiconductor during device fabrication.

Metal/semiconductor (MS) interface

A schematic view of the band diagram of the MS interaction is shown in Figure 6.2. The work function difference between the metal and semiconductor gives rise to a Schottky contact. According to the Schottky-Mott model, the barrier height (Φ_b) is determined by the difference between the metal work function (Φ_m) and the semiconductor electron affinity (χ_s) as follows:

$$\Phi_b = \Phi_m - \chi_s \quad \dots 6.1$$

However, this model is only valid for the non-interacting Schottky barrier (SB) formation, as it does not emphasis on the MS interface properties. The carrier transport across the MS junction interface depends on applied bias and operating temperature, and dictated by carrier injection, trapping and carrier transport processes. In a Schottky contact, carrier injection rather than transport dominates the conduction properties.

Figure 6.2 Schematic of the formation of energy barrier at the metal-semiconductor interface.

Nanoscale contacts play vital role in the fabrication of nano-devices based on 1D semiconductor nanostructures such as single NW-FET based chemical and biological sensors.^{185, 186} Nanoscale effects such as; barrier width thinning is predicted by solving the Poisson, and an increase in tunneling current is experimentally observed.^{187, 188} In nanoscale contacts, Fermi-level pinning might be reduced for at the MS interface compared to their bulk counterparts¹⁸⁹.

6.1.2 Experimental Details

In₂O₃ NWs synthesis followed the similar procedure discussed previously in chapter 4, where the In₂O₃ nanowires were grown using VLS mechanism in a horizontal double quartz tube furnace at a source temperature of 900°C using Au as catalyst and In₂O₃ powder as the

precursor. OCD and SCD were fabricated using In_2O_3 nanowires from the same production batch. For the fabrication of OCDs, In_2O_3 NWs were first placed on the highly doped Si substrate deposited with 100 nm SiN_x which serves as the gate dielectric layer. Then the electrodes were selectively designed on top of the nanowires using conventional photolithography, where a positive photo resist (AZ 5312) layer of $\sim 1\ \mu\text{m}$ thickness was used to transfer the photo-mask patterns on an aligned nanowires on Si/ SiN_x substrate followed by the Cr (20 nm)\Au (50 nm) deposition in a dc sputtering system. The fabrication of SCDs followed the similar procedure except the nanowires were placed after the electrode deposition and formed on top of the electrode. All the devices were always heated at 200°C for 1 hr in air, before testing.

The electrical and gas sensing characterizations in both type of devices were performed on a Keithley 4200-SCS semiconductor characterization system, attached with an optical microscope and sensing gases with gas controller. The testing gases employed in this work were N_2 , CO (reducing) and NO (oxidizing). All the sensing experiments were performed at room temperature under 50 % RH.

6.1.3 Result and Discussion

The morphology of the as grown nanostructures is shown in Figure 6.3. The as-synthesized In_2O_3 nanowires were found to be single crystalline with preferred orientation along (111). Details regarding the morphology and crystallinity of the VLS grown circular nanowires can be obtained from chapter 4. In order to improve the sensitivity at room temperature, we have investigated sensing on two types of devices. In the first device, Schottky contacts at both ends of In_2O_3 NWs were made by placing NW on the Cr/Au electrode. In the second type of

device, In_2O_3 NWs were placed underneath the Cr/Au electrode for the Ohmic contacts at the two ends. Sensing towards 5 ppm CO and NO gases using both types of devices were studied.

Figure 6.3 Low and high magnification FESEM images of as synthesized In_2O_3 nanowire. Both images are captured in LABE (low angle backscattered electron) mode.

We have first examined the single nanowire resistors to explore the sensing performance using two terminal based devices. Device with a channel length of $\sim 10\ \mu\text{m}$ was used to detect NO_2 at room temperature in three cycles. Figure 6.4(a) shows the I-V measurements before and after the NO_2 exposure. Figure 6.4(b) shows the NO_2 sensing performance at room temperature. In the first cycle the sensor showed a sensor response of ~ 1.7 with a response and recovery time of ~ 14 min and 4 min. In the subsequent cycles the sensor response was reduced to ~ 1.4 with poorer recovery time of ~ 8 -10 min. The main problem with this device was slow response and recovery times. For more exposures the

recovery of the device to its initial baseline resistance was not obtained, which indicates the poor desorption of the attached gas molecule.

Figure 6.4 Single In_2O_3 nanowire resistor device, (a) shows I-V plot before and after NO_2 exposure, (b) 2 ppm NO_2 exposure in 3 cycles @ $V = 0.1$, at room temperature.

The poor surface kinetics in a resistor based nanowire device can be improved by applying an electric field at the gate in a NW-FET configuration. The field applied at the gate induces charge in the nanowire which improves the surface kinetics at the nanowire surface. Gate-refreshable FET devices is reported by *Fan et al.*¹⁹⁰ where an electric field through gate electrode was used to refresh the device. A NW-FET device with good transistor characteristics (such as high on-off ration, low sub threshold swing and higher mobility) is required to be a sensitive device at room temperature.

To examine the sensing capabilities of the single NW-FET devices, we first optimized the field gating effect by varying the gate voltage. As shown in Figure 6.5, a single In_2O_3 nanowire device with a threshold voltage of -24 V was used for sensing of 2 ppm NO_2 gas at

different gate voltages (from 10 V to -25 V). The device was found very sensitive in the sub threshold region with a maximum sensor response obtained at the threshold voltage range. When the gate voltage was set at the saturation current range, a minimal sensor response was observed. Our finding is in corroboration with the work reported by *Lieber et al.*⁸ where sub threshold regime was reported to have an optimal sensor response in a single NW-FET biosensor. In further experiments, we have applied the gate voltage in the sub threshold regime.

Figure 6.5 Gate voltage dependant sensor response (S) of 2 ppm NO_2 gas at room temperature and the typical I_d - V_g curve of the NW-FET.

Electrical measurements on the single nanowire OCD and SCD are shown in Figure 6.6 (a) and (b) respectively with devices possessing similar channel lengths of $\sim 4 \mu\text{m}$ and nanowire diameter of $\sim 165 \text{ nm}$ respectively. The corresponding electrical behavior of the

nanowire device can be observed clearly from the families of I-V plots. The OCD shows linear current-voltage (I-V) characteristics (Figure 6.6a). In case of SCD, an asymmetric and non-linear characteristics in both reverse and forward bias voltage was observed (Figure 6.6b).

Figure 6.6 I_d - V_d characteristics of, (a) single In_2O_3 nanowire device with nanowire underneath the electrode shows Ohmic nature of the contacts between the nanowire and electrode, (b) single In_2O_3 nanowire device with nanowire on top of the electrode, shows Schottky nature of the contacts between nanowire and electrode. Inset in both plots show the respective SEM images of the single nanowire device, the scale bar is 2 μm in both images.

These two above-mentioned device characteristics show that the change in electrical contact behavior has been achieved by placing the nanowire on top (SCD) or underneath (OCD) the electrode. When the nanowire is placed on the top of electrode, the contact material is gold and when the nanowire is underneath the electrode, the contact material is Cr (20 nm). Due to the different work functions of Cr (4.5 eV) and Au (5.1 eV - 5.47 eV), these devices form

different potential barrier for migration of electrons which results in the change of the contact resistance to In_2O_3 NW. In a NW-FET, gate electrode can be used for the thinning of Schottky barrier at the MS interface to increase the tunneling probability through thin barrier. Thinner barriers can produce larger tunneling currents. However, for undoped semiconductors tunneling does not contribute significantly at room temperature. I_d - V_g characteristics at a constant drain voltage $V_d = 0.5$ V has shown a threshold voltage of -13.6 V with a high on/off ratio of 1.5×10^6 and an electron mobility of $49.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was obtained from OCD (shown in supporting information S2). The details regarding formula used in mobility calculations can be found under section 6.2.

Figure 6.7(a) I_d - V_d characteristics measured on the single In_2O_3 nanowire device with nanowire on top of the electrode (Schottky device) at low temperature, (b) Arrhenius plot for the extraction of activation energy (0.35 eV in this case).

Low temperature I-V measurements were performed on SCD to extract the estimated activation barrier energy at the NW-electrode junction for thermionic electron current in the temperature range from 150 K to 297 K, with 0 V applied to the gate electrode. Figure 6.7(a)

shows the I-V characteristics at different temperature under a pressure of 10^{-6} mbar. Arrhenius equation $I_d \sim \exp [-E_a/kT]$ where E_a denotes activation energy, k denotes Boltzmann constant and T denotes the temperature, was used for the activation barrier energy extraction.¹⁹¹⁻¹⁹³ A typical Arrhenius plot in Figure 6.7(b) between I_d and $1/T$ at $V_d = 3$ V and $V_g = 0$ V was used to extract the negative slope for the barrier activation energy in the SCD. Activation barrier energy (E_a , for electrons) of 0.35 eV was obtained from the slope of Arrhenius plot for Au/ In_2O_3 NW FET, which was sufficient to produce rectifying behavior at room temperature. The dominant mechanism for current injection into the semiconductor in this case is thermal emission which gives an apparent height of the Schottky barrier. At lower temperature range, where $k_B T$ has smaller value, thermally activated carrier transport quenched and therefore larger V_d is needed to bring back the device to conductive state. Previously, Ti-Au/ In_2O_3 has revealed a small barrier height of 6.90 meV,¹⁹³ it is mainly due to the use of smaller work function of the contact metal Ti (4.33 eV) and a low k - gate dielectric SiO_2 . *S.N. Das et al.*¹⁸¹ have found Schottky barrier height (SBH) of 0.42 - 0.67 V for Pt/ ZnO single nanowire which exhibited a good rectifying behavior. The magnitude of the SBH is not solely dependent on the work functions of the materials used; other factors such as the contact area between semiconductor NW and metal electrode, and preparation of the metal-semiconductor interface also play a role in determining the magnitude of the SBH.

The gas sensing characteristics of the OCD and SCD towards CO and NO (which are reducing and oxidizing gases, respectively) were investigated under similar device conditions for both gases. The SCD was operated at a forward bias of $V_d = 3$ V and $V_g = -10$ V whereas OCD was operated at a forward bias of $V_d = 0.5$ V and $V_g = -10$ V for both types of gases.

Figure 6.8 Sensor response plots for 5 ppm CO gas at room temperature using, (a) OCD, shows weak response, (b) SCD, shows better response.

In the literature, most of the devices were composed of one end Schottky contact and were therefore operated in reverse bias mode.^{181, 85, 184} In this work, we have operated the device in forward bias mode because the device consist Schottky barrier at both ends of the nanowire. Figure 6.8(a and b) shows the sensor response towards 5 ppm CO by the OCD and SCD respectively. An increase in the sensing current was measured for several cycles of 5 ppm CO gas for both types of devices, but the sensor response of SCD was found to be nearly 4 times higher than OCD towards CO gas (Figure 6.8). The response and recovery time of OCD towards 5 ppm CO gas (52 and 10 seconds respectively) was slightly faster compared to 70 and 18 seconds of SCD correspondingly. Figure 6.9 (a and b) shows the sensor responses at room temperature towards 5 ppm NO gas using OCD and SCD respectively. The current in the device was found to be decreased for each cycle of 5 ppm NO gas. It can be observed from Figure 6.9(a) that the OCD shows high response (sensor response of ~30), which is almost 22 times higher than the SCD

Figure 6.9 Sensor response plots for 5 ppm NO gas at room temperature using, (a) OCD shows high response and inset shows the I_d -time plot for one cycle of 5 ppm NO gas, (b) SCD, shows poor response.

towards 5 ppm NO gas at room temperature. A response and recovery time of 160 and 25 seconds respectively was observed towards 5 ppm NO gas using OCD, indicating slow reaction kinetics. The low signal to noise ratio (S/N of 1.7) of SCD towards NO gas does not allow an accurate measurement of the response and recovery time. Surface chemical reaction kinetics strongly influences the response and recovery time constants of devices.¹⁹⁴ The response towards any chemical species depends on the ease of chemisorptions of their molecules on the NW and desorption of these molecules is associated with the resistance recovery. Thus the mean response and recovery times are defined by the adsorption and desorption rates of chemical species from the NW surface.

The schematic illustration of both types of devices and band diagrams before and after CO and NO exposure is shown in Figure 6.10. In each case, the increased barrier height after NO exposure is shown with the solid dash line and the lowering of barrier height after

CO exposure is shown in dotted dash line. The equivalent resistance circuit for a single nanowire in contact with the metal electrode at two ends was shown in Figure 6.10. Single NW FETs based sensor devices can be considered as three resistances made of R_{c1} , R_{ch} and R_{c2} connected in series (Figure 6.10c), where R_{c1} and R_{c2} are the contact resistances at the interface between metal/semiconductor at the two ends of the nanowire and R_{ch} is the nanowire channel resistance. The contact resistances R_{c1} and R_{c2} are large initially in the SCD devices which give a large equivalent resistance for the device, as a result small current flows across the interface. All three resistances dropped when CO gas was introduced into the chamber and increased for NO gas exposure resulting in a large change in the final value of equivalent resistance ($R_{c1} + R_{ch} + R_{c2}$) as they are connected in series.

6.1.3.1 Sensing Mechanism

The response of a conductometric nano-sensor is the change in the relative conductance of the device before and after the exposure to the detecting species. In order to obtain a better response, it is advantageous to start with a device which can give a higher relative change in the device conductance. In a single NW device, there are mainly two components (nanowire channel conductance and contact resistance at the two junctions) which play a major role in the output of the device. Out of these two components, the nature of contacts at the junction play dominant role in the device output. If the contacts are rectifying type (SCD) then the modulation in the SBH due to the gas molecules interaction at the MS interface during sensing plays an important role in the sensor response. In a moderately doped semiconductor, at low bias values the conduction properties are limited by carrier injection over the barrier at MS interface. For the non-rectifying type of contacts (OCD), main contribution comes from

the change in nanowire channel conductance during sensing due to the electronic exchange between channel and adsorbed gas molecule on the channel.

Figure 6.10 Schematics of (a) SCD (b) OCD (c) electrical resistance equivalent circuit of the device (d) band bending in SCD with SBH modulations after the NO and CO gas exposure and (e) band diagram of the OCD, at zero bias voltage.

Reducing gases (e.g. CO) are electron donating in nature, their exposure lead to enhanced conductivity of the n-type semiconductor channel device. In the exposure of CO

gas to the OCD (where SBH is nearly zero), the sensor response was found to be mainly due to the change in the channel conductivity which is expected to be smaller due to limited surface chemical reaction kinetics at room temperature.^{194, 195} However, if CO is exposed to SCD (with an arbitrary SBH), the sensor response is contributed by both the change in the channel conductance and reduction in SBH (due to the adsorption of the gas molecule at MS interface) which show a larger response than the previous case. Due to the lowering of barrier height when CO gas was exposed to SCD, a larger change in conductance of the device was observed.

On the other hand, after the exposure of another class of gases e.g. NO (oxidizing gas, which has an electron withdrawing nature) to an OCD, it is expected a drop in device conductance due to its electron withdrawing nature of the gases of this class. In OCD, due to the small contact resistance, the sensor response is mainly dependent on the change in channel conductance. With the electron withdrawing nature of the oxidizing gas molecules, a small down shift in the Fermi level occurs as a result a slow decrease in the device conductance was observed. In the undoped In_2O_3 nanowires due to the low charge carrier concentration, exposure to NO gas forms an electron depletion region near the surface. Adsorption of gas molecules on the nanowire surface induces charge transfer which may affect the carrier concentration and mobility of the nanowire.¹⁹⁶ As NO gas was exposed to the SCD, a low response was shown by the sensor (Figure 6.9b) compared to the previous case (Figure 6.9a). In SCD, there is an arbitrary SBH before the commencement of sensing operation. When NO gas is exposed to such devices, there is a further increase in the barrier height at the junction, which allows even lesser charge carriers to migrate through the barrier. As a result, the SCD shows poor response to NO gas.

In the schematic of the band diagram of OCD (Figure 6.10e), a small resistance barrier is shown for OCD, this may exist because of the surface oxygen adsorption on the undoped In_2O_3 NW which withdraws electrons from the nanowire and form negatively charged oxygen ions that results in a small depletion region formation on the nanowire surface. When NO gas is exposed to the OCD, the electron depletion region extends further into the nanowire bulk which causes a further increase in potential barrier. For a smaller fixed applied voltage (0.5 V) during sensing, it is difficult for the charge carriers to overcome the barrier and the current gradually reduces with increasing NO exposure time. In the case of CO gas exposure to OCD, there is an increase in the electron concentration in the nanowire channel due to the conversion of CO into CO_2 ($\text{CO} + \text{O}_2^- = \text{CO}_2 + \text{e}^-$) resulting in a slight decrease in the depletion region with a lowering of the barrier height. However, the change in relative current is very small due to the nearly saturation current flowing in the OCD. As a result, the relative change in current before and after CO exposure in the OCD is smaller compared to the relative change in current during NO gas exposure.

In SCD, large resistance barriers exist at the two ends of the nanowire, electrons required a larger energy to overcome the barrier, consequently, a larger voltage is required to initiate the flow of electrons in the device. When CO gas is exposed to the SCD in such initial conditions (with larger voltage ~ 3 V), there is a large increase in the current. In such initial conditions, even a small lowering of the barrier height can make the electrons travel across the barrier resulting in drastic current change. On the other hand, NO gas exposure further increases the resistance barrier in SCD, leading to a small noisy decrease in current.

The modulation of contact resistance during gas exposure at the MS interface plays a crucial and dominant role to define the gas mechanism in SCD; meanwhile the kinetics of

gas-surface chemical reactions at the solid-gas interface governs the electronic interaction between gas molecule and NW. Surface reaction kinetics depends strongly on temperature,¹⁹⁴ partial pressure of the gas in the chamber,¹⁹⁵ surface properties and surface oxygen vacancies of the material used.¹⁹⁷ Considering that both the devices contain similar surface and structural properties [e.g. nanowire channel area made of the same material, surface properties (oxygen vacancies and other defects)], with the same operational parameters [e.g. temperature, humidity, gas flow rate (300 sccm)], similar surface kinetics can be considered. The key difference is the contact resistance at the two ends of the devices and hence operating voltages. Higher operating voltage of SCD (3 V compared to 0.5 V of OCD) makes a difference in the electric field (voltage per unit length). Despite a higher electric field (in SCD) that will sweep electron faster ($F = qE$) in the SCD, the larger energy barriers at the junction in a SCD does not allow instantaneously fast response as an output. The surface chemical kinetics play a dominant role in the OCD, as there are small energy barriers at the MS junction. Therefore, any change in the carrier concentration instantly reflects as an output in OCD giving a fast response. The larger energy barriers at the MS interface in SCD dominate the device output response.

6.1.4 Summary

In summary, utilization of contact resistance has been demonstrated as an effective way to improve the sensor response for two different classes of gas at room temperature. When nanowires placements are located on top of the electrodes, it showed SCD characteristics. Temperature-dependent I-V results show that the thermal emission contributes significantly in the carrier transport with an activation barrier of 0.35 eV. In contrast, when nanowires

were placed underneath the electrodes, it showed OCD characteristics. These two different types of devices have been found useful for two different classes of gases; OCD exhibits a large response for the oxidizing gases (e.g. NO) and SCD devices shows better response for reducing gases. In OCD, main contribution to sensor response comes from the nanowire channel and in SCD, modulation of SBH dominates the contribution. Achieving high sensor response by utilizing contact resistance at the MS interface suggests the possibility of using these devices at room temperature for a particular class of gases with distinct response. This work delineates the importance of device type selection for a particular class of gas with higher response. This work is the basis for our further device testing. To enhance the sensitivity, we have further tested reducing gases on the SCD with nanowire functionalization which is discussed in the next chapter. Zn-doping has been performed in to In_2O_3 nanowires to improve the sensor response and is discussed in the next section.

6.2 Zn doped In₂O₃ NW-FET based sensors

This section describes the role of doping into the nanowire channel in a single NW-FET configuration on the sensor response. We have tested CO gas after Zn-doping into the In₂O₃ nanowires using an OCD. Room temperature sensing of CO gas (1 -5 ppm) using high performance single Zn-doped In₂O₃ (Zn-In₂O₃) NW-FETs is demonstrated. Zn was chosen for the doping in In₂O₃ mainly because Zn-insertion (divalent) has been found to improve the NW-FET characteristic which is discussed later in this section. Zn-In₂O₃ nanowires were grown in a horizontal CVD furnace; single Zn-In₂O₃ NW-FETs were fabricated using SiN_x dielectric layer and bottom gate. NW-FETs characterization showed high performance devices, with a high “ON” current of 8×10^{-6} A at a 5 V drain voltage, high drain current on-off ratio of $\sim 10^6$ and electron mobility of $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Zn-In₂O₃ NWs are found to be enhancing the sensor response compared to pure In₂O₃ nanowire. Selectivity of CO gas over NO and NO₂ gases are also achieved by using Zn-In₂O₃ NWs. A negative threshold voltage shift of -3.5 V is observed just after exposure to 5 ppm CO gas. This approach represents an important step forward towards the room temperature sensing of hazardous gas.

6.2.1 Introduction

Most of the resistor based chemical sensors show poor response at low or near room temperature. Single or network based FET devices have shown possible room temperature sensing operation with higher sensor response for NO₂.²⁸ Researchers of this community have used different approaches to improve the sensor response at near room temperature. Approaches including foreign atom doping, microstructure control, channel functionalization

etc. have been adapted to MOx based chemical sensors.^{198, 147} Adsorption-desorption kinetics of the gas molecules at the nanowire surface defines the sensor response for a particular chemical species. The adsorption kinetics of chemical species at the nanowire surface can be tuned by decorating the nanowire with metal nanoparticles or by doping with an element having a stronger chemical affinity for a particular chemical species. Doping into the nanowire have been found to create defects such as oxygen vacancies etc., and these defects act as preferential adsorption sites for chemical species (e.g. gas molecules) which lowers the operating temperature.¹⁹⁹

CO is one of the major pollutant gases in the environment and is mostly produced by the automobiles and industrial processes. It adversely affects human health at only a few parts per million. In the literature, CO gas detection limit has been limited to 4-10 ppm with low sensor response even at elevated operating temperature.^{200, 201} Ppb level detection of CO gas using SnO_x-Pb nanoparticles at 350°C has been reported by *Aruna et al.*⁸⁴ and at room temperature *Joshi et al.*²⁰² have reported a detection of 100 ppm CO gas by utilizing gold nanoparticle immobilization on ZnO nanowires. There is a strong need to develop a sensor device which can detect CO in sub 10 ppm concentration level or below for environmental monitoring or home-land security applications.

6.2.2 Experimental Details

Zn-In₂O₃ NWs were grown in a horizontal CVD furnace at a source temperature of 900°C, the details growth procedure of nanowires can be found at chapter 4. In briefly, the source for the growth was taken as a mixture of ZnO and In₂O₃ powders with graphite powder. During

the deposition, argon gas flow rate was fixed at 50 sccm and the pressure inside the quartz tube was maintained at 1 mbar. Si substrates with 9 nm gold layer were kept downstream and the substrate temperature ranges from 400-550°C with deposition duration of 60 min. The as grown Zn-In₂O₃ samples were then annealed at 300°C for 2 hours in atmosphere.

Morphological and elemental characterizations detail can be found in chapter 4. Photoluminescence studies were carried out at room temperature on a Cary Eclipse EL system at an excitation wavelength of 264 nm. The device fabrication of Zn- In₂O₃ nanowire followed similar procedure as discussed in the previous section 6.1, chapter 6. All the electrical and sensing measurements on the single NW-FET devices were performed at room temperature on a probe station attached with Keithley 4200-SCS semiconductor characterization system, optical microscope and sensing gases with gas controller at a RH level of 50%.

6.2.3 Result and Discussion

The typical morphology of the as grown Zn-In₂O₃ NWs is shown in Figure 6.11(a and b). The presence of the Au catalyst at the nanowire apex indicates the VLS growth mechanism. As shown in the FESEM images, the as-grown nanowires have a diameter of 50-300 nm and a length of 10-30 μ m with circular cross-section. Figure 6.11 (c) shows a HRTEM image of the nanowire with an interplanar distance of 0.70 nm for {110} when viewing along <111>. The SAD (in the inset of Figure 6.11c) pattern was taken along [111] zone-axis and indexed accordingly, which reveals that the nanowire has single crystalline cubic structure. In Figure 6.11(d), the EDS pattern measured on a single Zn-In₂O₃ NW showed a weak Zn peak with 1.6 at% Zn inclusion in the In₂O₃ NW. It has been reported that the solubility of Zn in the

In_2O_3 lattice is low,²⁰³ which agrees well with our result. In addition, we have observed a shift in the XRD peaks (Figure 6.12) towards higher theta value, which confirms the presence of Zn in the In_2O_3 lattice.

Figure 6.11 Images of; (a, b) as grown Zn-In₂O₃ NW under low and high magnification FESEM, both the images are taken in the low angle back scattered electron detection (LBE) mode. Figure (c) shows HRTEM image of the Zn-In₂O₃ NW, depicting a family of {110} planes with inter planar distance of 0.71 nm. In the inset SAD pattern is indexed and taken along [111] zone axis, and (d) shows the EDS pattern which was measured on a single Zn-In₂O₃ NW, showing a series of In, O and weak Zn peaks

Figure 6.12 XRD patterns of (a) undoped and Zn-doped In_2O_3 nanowires and (b) shows the closely investigated In_2O_3 (222) peak where a higher 2θ shift after Zn-doping was observed

X-ray photoelectron spectroscopy:

In order to investigate the composition of the Zn doped and undoped In_2O_3 nanowires, XPS measurements were carried out. Figure 6.13 shows the XPS patterns for both devices, depict the full range scanned from 0 to 1100 eV. Peaks such as C, O_{1s} , In_{3p} , In_{3d} , In_{3s} , In_{4p} , Zn_{2p} etc.

were detected. A weak Zn_{2p} peak was observed from the $\text{Zn-In}_2\text{O}_3$ sample, and it could be due to the low Zn insertion into the In_2O_3 nanostructures.

Figure 6.13 XPS patterns measured from In_2O_3 and $\text{Zn-In}_2\text{O}_3$ nanowires. Mg K_α X-ray (1253.6 eV) was used to analyze the samples.

The detailed analysis of In_{3d} and O_{1s} peaks are shown in Figure 6.14. Each of the In_{3d} and O_{1s} XPS signals of both the samples can be deconvoluted into two components. For In_{3d} signals two Gauss–Lorentz (GL30) peaks with each of the associated signal were deconvoluted with the same full width at half maximum (FWHM) (Table 6.1). The doublet in each of the signal (in both materials) indicating the presence of two In sites of different chemical environments.

One of the possibilities is due to the bonding to different oxygen atoms (e.g. In_2O_3 , $\text{In}_2\text{O}_{3-x}$ or InO) which indicates oxygen deficient nanostructures.

Figure 6.14 Detailed analysis of In_{3d} XPS peak for (a) $\text{Zn-In}_2\text{O}_3$ and (b) In_2O_3 and O1s peaks for (c) $\text{Zn-In}_2\text{O}_3$ and (d) In_2O_3 .

Table 6.1 Details of In_{3d} peak measured from Zn- In_2O_3 and In_2O_3 nanowires:

	Zn-In ₂ O ₃				In ₂ O ₃			
Peak	In3d _{5/2}		In3d _{3/2}		In3d _{5/2}		In3d _{3/2}	
Splitting	7.60				7.53			
Position	444.45	444.98	452.11	453.14	444.52	445.37	452.16	453.01
FWHM	1.55	2.11	1.55	2.11	1.50	2.16	1.50	2.16
Area	11807.1	9357.3	8641.4	3690.9	10945.1	12320.1	7535.2	7154.4

The corresponding details (e.g. FWHM, peak position, peak splitting etc.) related to each peak are summarized in Tables 6.1 and 6.2. The observed O_{1s} peak at 530.05–530.22 eV can be assigned to lattice oxygen in In_2O_3 .¹⁵⁰ The second peak observed at 532.12 eV (for Zn- In_2O_3) and 531.57 (for In_2O_3) is assigned to the presence of water at the nanowire surface as its binding energy falls in the range of 531.5 eV(OH) and 533 eV (H_2O).²⁰⁴ Larger peak splitting (O_{1s} doublet, 2.7 eV for Zn- In_2O_3 and 1.35 eV for In_2O_3) for Zn- In_2O_3 indicates the Zn doping into the In_2O_3 crystal system.

Table 6.2 Details of O_{1s} peaks measured from $Zn-In_2O_3$ and In_2O_3 nanowires:

Peak (O_{1s})	$Zn-In_2O_3$		In_2O_3	
Positions	530.05 (O^{2-})	532.12 (O_2^{2-})	530.22	531.57
Separation	2.7 eV		1.35 eV	
FWHM	1.52	2.79	1.45	2.77
Area	2700.7	4186.1	3073.0	6034.7

Figure 6.15(a) shows a schematic illustration of single NW-FET device used in this study. $Zn-In_2O_3$ nanowires (with 1.6 at% Zn) were placed on the patterned source and drain electrodes with 60 nm SiN_x high-k gate dielectric layer on highly doped n- type Si substrate served as a back gate electrode and the chemical sensor device was realized using this FET based sensor configuration. A representative FESEM image of the single $Zn-In_2O_3$ NW bridging between two electrodes with a channel length of 18 μm is shown in the inset of Figure 6.15(b). Similar NW-FET devices were fabricated using the undoped In_2O_3 NWs.

Figure 6.15(a) Schematic diagram of NW-FET, with Cr (10 nm)\Au (50 nm) serving as electrodes, SiN_x serving as gate electrode and highly doped (resistivity 0.005 Ω-cm) n-type Si as back gate, (b) FESEM image of a array of devices and in the inset a single NW-FET device.

Figure 6.16 Electrical measurements done on the single NW-FET; (a) family of drain current- voltage (I_d - V_d) characteristics at different gate voltage (v_g), (b) I_d - V_g curve before and after 5 ppm CO gas exposure, showing a negative threshold voltage shift after exposure to CO gas for 1500 seconds.

It is important and advantageous to realize highly functional NW-FET devices for the purpose of optimizing sensing properties. Zn-In₂O₃ NW-FETs are found to show remarkable n-type FET characteristics.^{50, 203} In this work, the transport properties of single NW-FET device exhibited excellent n-type characteristics with strong gate control. The I_d-V_d characteristics were performed on a single nanowire as shown in Figure 6.16(a), indicates a good conductivity of the nanowire with a high “ON” state current of 8×10^{-6} A at 5 V drain voltage (V_d). Figure 6.16(b) shows the I_d-V_g curve recorded from the same device at V_d = 5 V, with a linear behavior above a threshold voltage V_T of -15.65 V. A sub-threshold swing value of ~140 mV/decade and a drain-source current on/off ratio $\sim 1 \times 10^6$ can be achieved, which are comparable to one of the best reported values.²⁰³ The electron mobility (μ_e) was determined to be $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the linear operation region using the equation $\mu = (1/C)[g_m](L^2/V_d)$;²¹ where, g_m is the transconductance (2.216 μS), L is the nanowire channel length (18 μm) and $C = 2\pi\epsilon\epsilon_0 L / \cosh^{-1}(1+h/r)$ is the approximate nanowire capacitance; where ϵ is the dielectric constant of Si₃N₄ (~7), h is the thickness of the Si₃N₄ layer (60 nm), and r is the radius of the nanowire (125 nm). For the undoped single In₂O₃ NW-FET a threshold voltage of -21.5 V, an “ON” state current of 8.5×10^{-6} A with an on/off current ratio of 5×10^5 was measured at 5 V drain voltage.

The Zn-In₂O₃ NW-FET sensors were used for the detection of pollutant CO gas at room temperature. The system was first purged with N₂ gas to remove the excessive oxygen species from the surface of the nanowire and chamber. There was a slight current increment during the N₂ purge due to the partial desorption of the ionized oxygen species from the nanowire surface. Drain voltage (V_d) was kept constant at 3 V and gate voltage (V_g) was kept constant at -15 V (which is in the threshold region of the NW-FET) during the

measurements. The response of the Zn-In₂O₃ NW sensor for 1-5 ppm CO gas is shown in Figure 6.17(a). The change in the current for 1 ppm CO gas was not as significant as for 2 ppm and above (Figure 6.17a). We can detect distinct electrical changes for the CO gas concentration down to 2 ppm using these Zn-In₂O₃ NW sensors at room temperature. An increase in sensing current can be observed during CO gas exposure (Figure 6.17b). As shown in Figure 6.18, the sensor response plot of the Zn-In₂O₃ NW sensor for 5 ppm CO gas shows a response time of 20 seconds and recovery time of 10 seconds. The sensor response of ~1.65 was obtained from Zn-In₂O₃ (Figure 6.18), which is better than ~1.05 of the undoped In₂O₃ (Figure 6.8a).

Figure 6.17 Room temperature gas testing characteristics of; (a) Zn-In₂O₃ NW-FET sensor at different CO gas concentrations, and (b) Zn-In₂O₃ NW-FET sensor during 5 ppm CO gas exposure in four different cycles.

In order to examine the selectivity of the Zn-In₂O₃ NW-FET for CO gas, other pollutant gases such as NO and NO₂ were tested under the same operating conditions of

drain bias voltage of 3 V and gate voltage $V_g = -15$ V. The response of the Zn-In₂O₃ NW sensor compared to different gases is shown in Figure 6.19. It is evidently shown that the Zn doped NW sensors attained a good selectivity of CO gas over NO and NO₂ at room temperature, despite a moderate response (30%) for 2 ppm NO₂ (which is considered as a highly oxidizing gas and has a threshold limit in sub ppb range). A negative threshold voltage (V_T) shift of ~ 3.5 V was measured after 5 ppm CO gas exposure at room temperature.

Figure 6.18 Sensor response plot of the Zn-In₂O₃ NW sensor for single cycle of 5 ppm CO gas, showing a response time of 20 seconds and recovery time of 10 seconds

This negative shift in threshold voltage can be explained in terms of the change in carrier concentration. After CO gas exposure, an increase in the electrons concentration is expected in an n-type semiconductor due to the electron donating nature of the reducing gases (e.g. CO). CO oxidized in to CO₂ ($\text{CO} + \text{O}^- \rightarrow \text{CO}_2 + \text{e}^-$) after interaction with the chemisorbed oxygen species at the nanowire surface. Thus, electrons are released into the nanowire. As a

result, the increased electron concentration leads to a negative shift in the threshold voltage after exposure to CO gas.

Figure 6.19 Response of single Zn-In₂O₃ NW sensor to the different gases (5 ppm CO, 5 ppm NO and 2 ppm NO₂) at a fixed $V_d = 3$ V and $V_g = -15$ V, sensor was operated at room temperature.

As we have observed and discussed in the beginning of the result and discussion section that during sensing, it is important to maintain the gate voltage (V_g) in the threshold region in order to obtain the optimized sensor response.

6.2.3.1 Sensing Mechanism

There are two main effects of doping in MOx nanowires; firstly, change in electronic conductivity and secondly, the introduction of defects into the nanowire system. These both factors affect the sensor response. Defects within the crystal structure can improve the adsorption of gas molecules on the nanowire surface¹⁹⁹ and the change in the conductivity

will change the position of Fermi level in the energy band diagram which governs the electronic transportation between gas molecule and nanowire material. In conductometric gas sensors, surface reaction kinetics between gas molecule and nanowire surface play a vital role in defining the sensing parameters. In this work, it is unlikely that solely chemical affinity between Zn and CO can lead to the significant CO gas detection enhancement mainly due to the small amount of Zn insertion (~ 1.6 at%) into the nanowires.

Figure 6.20 PL spectrum obtained at room temperature from the as deposited undoped and Zn- In_2O_3 NWs with an excitation wavelength of 264 nm.

A plausible explanation on the improved sensing behavior in the doped semiconductor compared to undoped nanowires is related to the defects created by doping. Doping in nanowires can generate defects such as oxygen vacancies, metal interstitials, and surface defects etc.^{60, 205} These defects play a vital role in the sensing of CO gas. The defects generated can be evaluated based on the PL spectrum (shown in Figure 6.20) taken from the Zn-doped and undoped In_2O_3 NWs under the excited wavelength of 264 nm of a Xe lamp. A

series of PL peaks (420 nm, 445 nm, 460 nm and 485 nm) belonging to different types of defects^{206, 205} can be found. Additional PL peaks (420 nm and 445 nm) have been observed from the Zn-doped sample. These extra peaks can be attributed to the neutral and ionized oxygen vacancies (V_o , $V_o^\bullet$ and $V_o^{\bullet\bullet}$) and metal vacancies ($V_{In}^\bullet$) created by Zn-doping at high processing temperature.²⁰⁵ Hsin *et al.* have reported that Zn doping in In_2O_3 nanowires increases oxygen vacancies, as a result green emission was observed to be enhanced and UV emission was depressed. Most of the defects can play a role of as the preferential adsorption site for a gas molecule.¹⁹⁹ We suggest that this promotes the activation of doped nanowires even at room temperature when reacting with the testing gas.

Zn-doping has been observed to shrink the band gap from ~ 3.75 to ~ 3.3 eV when characterized by UV-VIS spectroscopy (Figure 6.21). Similar red shift in the optical band gap of ZnO doped with transition metal is explained by exchange interaction between conduction band electrons of ZnO and localized $3d$ electrons of substitutional transition metal ions.^{207, 208}

Figure 6.21 UV-Vis spectra measured from Zn-In₂O₃ and pristine In₂O₃ nanowires.

Electronic transport between nanowire and CO gas molecule can be explained in terms of the transfer of electrons from CO gas molecule to the nanowire due to the chemical potential gradient ($\Delta\mu$) between semiconducting In_2O_3 nanowire and CO molecule.¹⁴⁷ It is well known that as grown In_2O_3 behaves as n-type semiconductor due to the existence of the native defects (metal interstitials, oxygen vacancies) in it. In the energy band diagram, the resultant position of E_F is nearer to E_C for undoped In_2O_3 (shown in Figure 6.22a) where E_C , E_v and E_F correspond to the conduction band, the valence band and the Fermi level of the In_2O_3 NWs. After Zn-doping, there is a slight increase (due to the low 1.6 at% Zn insertion) in the resistance (supporting information S₃) but overall the nature of the Zn- In_2O_3 NW still remains n-type. In the band diagram for Zn- In_2O_3 NW, E_F can be slightly shifted towards E_v (Figure 6.22b) compared to undoped In_2O_3 band diagram (Figure 6.22a). A chemical potential level μ_{co} , represents the chemical potential CO molecule that participates in the electron transfer process.

Figure 6.22 Energy band diagram of, (a) undoped In_2O_3 , a n-type semiconductor, (b) Zn- In_2O_3 , a less n-type semiconductor with E_F moved slightly towards E_v compared to undoped In_2O_3 . μ_{co} represents the chemical potentials of the CO molecule.

In metal oxides, oxygen chemisorption on the nanowire surface creates an electron depletion layer at/near the surface which results in energy band bending near the surface (as shown in

Figure 6.22). When CO molecules adsorb onto the In_2O_3 NW surface, electrons transfer start from a higher chemical potential to the material with a lower chemical potential until the system reaches equilibrium. For the samples with undoped In_2O_3 NW, there is a smaller chemical potential gradient between the adsorbed CO molecule and the undoped In_2O_3 compared to the Zn- In_2O_3 . This results in the lesser electron transfer (to reach equilibrium) and therefore slow sensor response output with lower sensitivity for the undoped In_2O_3 NWs. On the other hand, the larger difference in the chemical potential of the CO molecule and Zn- In_2O_3 NW gives us faster (response time 20 sec. and recovery time 10 sec.) and larger transfer of electrons, hence better sensor response can be achieved. The band gap contraction after Zn-doping also contributes to the larger chemical potential difference between CO molecule and Zn- In_2O_3 .

6.2.3.1.1 Kelvin probe force microscopy:

Figure 6.23(a) Topography and (b) surface potential profiles of pure single In_2O_3 nanowire.

To understand the downshift in the Fermi level, we have measured the surface potential (SP) profiles of Zn-doped and undoped In_2O_3 nanowires by Kelvin probe force microscopy

(KPFM) method in a scanning probe microscope. In KPFM, a contact potential difference (CPD) appears as a consequence of contrast in work function between the tip and the sample, as a result of CPD appearance an electrostatic force established between the tip and the sample. An external DC voltage is applied to compensate this electrostatic force. KPFM technique is able to measure the work function of the nanomaterials surface locally. Figure 6.23 and Figure 6.24 show the SP profiles measured on a single In_2O_3 and $\text{Zn-In}_2\text{O}_3$ nanowire respectively. A fixed DC bias of 2 V was used to measure the SP of nanowire in semi-contact mode. A surface potential contrast (between nanowire and Au background) of ~ 14 mV and ~ 80 mV from the undoped and $\text{Zn-In}_2\text{O}_3$ were measured respectively (Figure 6.25). The detailed line profiles measured across the nanowires (to measure the surface potential contrast of the nanowire and background) are shown in Figure 6.25. Since the surface potential is directly proportional to the work function of the material and in semiconductors, work function is related to the Fermi energy level (E_F).

Figure 6.24 (a) Topography and (b) surface potential profiles of pure $\text{Zn-In}_2\text{O}_3$ nanowire.

According to the definition of work function, the differences in the work function contrast $\Delta\Phi$ (or SP contrast) are directly related to the difference in the Fermi levels (ΔE_F) of the materials (as shown in Figure 6.26). Thus, a relative Fermi level downshift (ΔE_F) of ~ 65 meV was measured from the SP images after Zn doping.

Figure 6.25 Line profiles on the surface potential images of, (a & b) In_2O_3 nanowire, and (c & d) of Zn- In_2O_3 nanowire, respectively.

Figure 6.26 Depiction of the Fermi level shift after Zn-doping in to In₂O₃.

Apart from existing chemical potential gradient, there are other factors such as; nanowire preparation conditions, overall device conductivity, surface reaction kinetics, and the device operating conditions etc. which contribute to enhance the sensor response. To maintain the charge balance, the divalent doping of Zn²⁺ generates excess lattice oxygen-ion vacancies, which has two distinct effects. Firstly, Zn-doping improves receptor function by increasing the surface oxygen chemisorptions. Secondly, it improves transducer function of the device by enlarging the space-charge layer thickness at the nanowire surface. Thus, the effective channel width of the nanowire channel reduces and the device becomes more sensitive. Hence, the Zn-doping improves both the receptor and the transducer functions of the NW-FET sensor configuration at room temperature.

These findings are in agreement with the sensing results we have discussed in chapter 5, where Zn-doped In₂O₃ nanowires network resistor devices have shown enhanced

sensitivity towards reducing gases (e.g. CO) gas at higher operating temperature. Zn-doped In_2O_3 NW-FET based devices have also shown enhanced sensitivity towards CO gas at room temperature.

6.2.4 Summary

Zn- In_2O_3 NW channel in NW-FETs are shown potential candidates for room temperature detection of CO gas. Zn- In_2O_3 based NW-FETs showed excellent electrical and electronic characteristics including, a high “ON” state current, high on-off modulation ratio of 10^6 , a high on-state current of 8×10^{-6} A at $V_d = 5$ V, a small sub-threshold gate voltage swing of 140 mV/decade and an electron mobility of $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Such highly operating NW-FET has shown promising sensing properties for 1-5 ppm CO gas at room temperature. Due to electron donating nature of the CO gas, a negative threshold voltage shift of -3.5 V was also observed after exposure to 5 ppm CO gas. In addition, a good selectivity over NO and NO_2 gases were also observed which is correlated to the defects generated and the Fermi level shifting in a Zn- In_2O_3 NW due to the Zn-doping.

Chapter 7

Au-NPs -Functionalized In₂O₃ Nanowires

In the previous chapter, we have noted that the Schottky contacted devices have shown better sensor response for CO gas at room temperature. In order to further improve the sensor response, the Schottky contact effect can be coupled with the nanowire channel functionalization with metal nanoparticles. Metal nanoparticles can enhance the catalytic oxidation of CO gas on the nanowire surface which will improve the sensitivity at room temperature. In this chapter, room temperature sensing of CO gas using gold nanoparticles (AuNPs) functionalized In₂O₃ NW-FET is presented. AuNPs were functionalized onto In₂O₃ nanowires *via* a self assembled monolayer of *p*-amino-phenyl-tri-methoxy-silane (APhS-SAM). The nanowires were mounted onto the Au electrodes with both ends in Schottky contacts. High sensor response towards low concentration of CO gas (200 ppb-5 ppm) at room temperature is achieved. AuNPs on the nanowire surface serve to enhance the CO oxidation due to a higher oxygen ion-chemisorption on the conductive AuNP surfaces. Detailed studies showed that the sensing capabilities were greatly enhanced in comparison to those of bare nanowires or low coverage of Au NPs decorated nanowires. The CO molecules interact with the pre-adsorbed oxygen ions on the AuNP surface during CO gas exposure. The CO oxidation on the AuNPs leads to the transfer of electrons into the semiconducting In₂O₃ nanowires and this is reflected as the change in conductance of the NWFET sensor.

This work provides a promising approach for fabricating nanowire devices with excellent sensing capabilities at room temperature.

7.1 Introduction

In a chemical sensor, the sensing behavior critically depends on the reaction of the sensing material surface with the surrounding gases. To improve the selectivity towards CO, additional metal particles (e.g. Ag, Au, Pd, Pt etc.) have been often used as catalytic additives.²⁰⁹⁻²¹² The metal particles (Pt, Au, etc.)^{213, 214} on the metal oxide surface enhance the catalytic interaction of chemical species. Among the various metal catalyst particles, gold is the most widely used and explored catalyst for CO oxidation. Au atoms are known to be reactive for CO oxidation even at 30–40 K.²¹⁵ However, oxygen adsorption mechanisms on supported Au particle and activation are highly controversial. Several models have been proposed to resolve the controversy on the role of the support material. *Valden et al.*²¹⁶ proposed that oxygen adsorption proceeds directly on the Au particle. One of the widely accepted models proposed that the oxygen adsorption occurs at the metal–support interface,^{217, 218} possibly on oxygen vacancies,²¹⁹ which are present on MO_x such as TiO₂, Fe₃O₄, In₂O₃ or ZnO. Another model proposed that the chemisorbed oxygen on the metal oxide support dissociates very fast by producing lattice oxygen.⁸² These produced oxygen species subsequently react at the MS interface or after a spillover of oxygen to the Au.⁸²

Higher metal loading is required in order to achieve higher catalytic oxidation of CO. Different techniques have been used to achieve higher metal loading with uniform particle distribution. In order to explain the metal loading dependent *Kolmakov et al.*²²⁰ deposited Pd nanoparticles in an in-situ equipment. Simultaneously gas sensing experiments were

performed with different Pd loading. It was found that the sensor response strongly depends on the surface coverage of Pd particles. However, despite the higher coverage attained using in-situ deposition of metal particles, the non-selective deposition results in unavoidable deposition on the isolation region adjacent to the channel leading to extraneous conductive paths.²²⁰ This can affect drain current as a result of electron conductance when the metal nanoparticles exceed the percolation threshold. Self assemblies have been used in recent years to organize nanoparticles onto the surface of the nanowires.^{221, 222} Zhang *et al.*²²² have obtained a selective sensor response for low concentration of H₂S gas using ZnO nanowire modified with Pd nanoparticles through self assemblies.

The effectiveness in such catalysis systems depends on the nature of the interaction (weak or strong) between the support material and metal nanoparticle as illustrated in Figure 7.1. If the interaction between metal NP and support is weak (physical adsorption), then the catalysis depends on the size of the particle.^{223, 218} The catalytic reaction rate might be enhanced by spillover of the reactants by the metal NP. Boudart *et al.* reported an unexpected enhancement in CO sensing on Pd/Al₂O₃, due to the reverse spillover of CO to the metal from the support).¹⁶⁶

Figure 7.1 Schematic illustrations of the interactions between a novel metal nanoparticle and the support material. Nanoparticles with smaller sizes are advantageous due to (i) limited number of atoms present and (ii) more atoms at the nanoparticle surface and at the interface between support and nanoparticle.¹⁶⁶

In contrast, if the interactions between the support and the metal is strong (active support), the catalytic activities are also modified by the support. This can occur by electronic and chemical exchange between metal NP and oxide support. Examples of such active support systems are Au/Fe₂O₃, Au/TiO₂, Pd/SnO₂ etc.^{217, 220, 218} Kolmakov *et. al.*²²⁰ have reported an enhanced sensing response for hydrogen and oxygen gases from Pd/SnO₂ system. They have also reported the formation and modulation of nano Schottky junction barrier between oxide support and metal NP due to electronic exchange. As illustrated in Figure (7.2) electron depletion zones form around NPs resulting in a conductance drop follow by a band bending. They have attributed the enhanced sensor response to the modulation of the nano-Schottky barriers during the gas exposure. The chemical exchange

was explained in terms of the; first catalytic dissociation of molecular species into atomic by the metal NP followed by diffusion of atomic species in to metal oxide support. The above proposed mechanism (step 2 in Figure 7.2) is well known as the “spillover effect”.^{224-226, 220,}
²²⁷ The spillover zone area depends on the size of metal particle and other working conditions.

Figure 7.2(a) shows, schematic depiction of the processes at a MOx NW surface: (1) oxygen chemisorption at the defect sites of the MOx NW surface; (2) catalytic dissociation of molecular oxygen species on metal nanoparticles which leads to spillover of the atomic species onto the support MOx; (3) weakly adsorbed molecular oxygen captured by metal nanoparticle. These weakly adsorbed oxygen molecules diffuse along the MOx surface to the Pd nanoparticle’s vicinity (followed by process 2). R_s and R_c are the effective radii of the spillover, and collection zones respectively. Figure (b) depicts the band diagram of the MOx nanostructure and the band bending in the vicinity of metal nanoparticle [adopted from²²⁰].

Apart from the nanowire channel functionalization, sensor response in a NW-FET device also depends on the contact resistance at two ends of the nanowire. Contact resistance modulation in nanowire sensing has proved to be an effective way to improve gas sensing.²²⁸⁻²³⁰ In chapter 6, we have described that Schottky contact devices show a superior response to the reducing gas (CO), in agreement with other similar findings.^{228, 230} In this chapter, we describe the approaches of functionalization of nanowire channel by AuNPs on Schottky devices to enhance the sensor response towards CO gas sensing at room temperature. We have obtained highly sensitive devices for CO (down to ppb level) gas sensing at room temperature, one of the best reported performance for room temperature CO sensing.^{213, 231}

7.2 Experimental Details

7.2.1 Materials: *p*-aminophenyltrimethoxysilane (APhS) was purchased from Gelest, and used as received. Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) ($\geq 99.9\%$, Aldrich; *corrosive, handle with care*), sodium citrate (meeting USP testing specifications, Sigma), ethanol ($\geq 99.5\%$, Merck), toluene ($\geq 99\%$, Merck) and methanol ($\geq 99.5\%$, Merck) were used as received.

7.2.2 Synthesis of In_2O_3 nanowires: In_2O_3 NWs growth related details are given in the chapter 4. Similar operating conditions and materials have been also used in this work, to grow circular cross sectional nanowires at 900°C .

7.2.3 Synthesis of AuNPs: AuNPs were synthesized according to the method reported previously by *Grabar et al.*²³² Specifically, 0.012g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was mixed into 30 mL of deionized (DI) water in order to prepare 1 mM solution. Later, 6 mL of 38.8 mM

sodium citrate was dissolved in DI water was also added into the solution. The gradual change of color from grey to purple and finally to wine red indicates the formation of AuNPs.

7.2.4 Immobilization of AuNPs on In₂O₃ nanowires:

7.2.4.1 Substrate Preparation. In₂O₃ nanowires deposited on Si substrate was treated with 1:1:5 (v/v) mixture of 30 % hydrogen peroxide, 30 % (aq) NH₄OH and DI water at 75 °C for 45 min. Substrate was then copiously rinsed with deionized water, blown dry with nitrogen, and dried at 100 °C under vacuum for 30 min. This cleaning procedure creates a surface rich in hydroxyl groups at the In₂O₃ nanowires surface to facilitate the subsequent silanization process.^{233, 234}

7.2.4.2 Self-Assembly of aminosilane. Assembly of aminosilane was performed as described by Zhang *et al.*,²³⁵ wherein the hydroxyl terminated substrates were rinsed with toluene and then immersed in a 3 mM APhS solution in toluene for 2 h. Subsequently, after removing, the substrate was rinsed with toluene and then with acetone, finally blown dry with nitrogen.

Figure 7.3 Schematic for citrate capped AuNPs functionalization on In_2O_3 nanowire.

7.2.4.3 Immobilization of gold nanoparticles

The silane treated Si substrate was immersed in the freshly prepared AuNPs solution for 60 min; rinsed thoroughly with DI water and then baked at 110 °C for 5 min to remove residual moisture. Details schematic diagram of various deposition steps are shown in Figure 7.3.

7.2.5 Sensor device fabrication

In_2O_3 nanowire-based devices were fabricated on a highly doped n-type silicon wafer with a 100 nm SiN_x high-k dielectric layer. Standard optical-lithography followed by Cr/Au (10/50 nm) deposition and liftoff was used to define the contact electrodes. The highly conductive heavily doped Si substrate (resistivity 0.005 $\Omega\text{-cm}$) was used as a global back gate. The In_2O_3 nanowires were removed from the silicon substrates by sonication in Isopropyl alcohol (IPA)

solution. IPA solution containing In_2O_3 nanowires and AuNPs functionalized In_2O_3 nanowires were drop-casted onto the patterned Si substrate. Single nanowires were aligned using DEP method. After drying, locations of nanowires on the pads (electrodes) were identified for fabricating single nanowire-based FET structures. Electrical and sensing measurements on the nanowire FET were done in a Keithley 4200-SCS semiconductor characterization system, attached with an optical microscope and sensing gases with gas controller. I_d - V_d transistor characteristics on a single NW-FET were performed under different applied V_g ranges from 5 V to -15 V with a voltage step of -5 V. In I_d - V_g transistor characteristics, I_d was measured for a range of V_g (-10 to 5 V) under a constant applied V_d bias of 2 V. The responses of the NW-FET device to CO gas were evaluated by measuring the resistance/conductance change upon exposure to various concentrations of CO gas in a dynamic gas flow chamber under a constant gas flow rate of 300 sccm. Various concentrations of CO gas were obtained by diluting a premixed concentration of CO gas in N_2 .

7.3 Results and Discussion

APhS-SAM layer was used to functionalize the AuNPs on the nanowire surface. As shown in the FESEM image (Figure 7.4a), the as-grown nanowires have a diameter of 150-200 nm and Figure 7.4(b) shows FESEM image after functionalization of the citrate stabilized AuNPs on APhS-SAM treated In_2O_3 nanowires. AuNPs were functionalized on amine terminated surface due to amine-gold interaction.

Figure 7.4 FESEM images of (a) as synthesized In_2O_3 nanowires and (b) AuNPs functionalized In_2O_3 nanowires. TEM images of (c) AuNPs functionalized In_2O_3 nanowires using SAM layer and (d) AuNPs decorated In_2O_3 nanowires without SAM layer.

Figure 7.5 TEM images of the nanowires with different Au loading time during immobilization. The scale bars in all images are 100 nm.

The nanowires show a high coverage of AuNPs with sizes of around 10 nm as shown in the TEM image (inset of Figure 7.4c). To evaluate the effect of AuNPs coverage on nanowire surface, we have fabricated two types of devices: in the first type of devices, an APhS-SAM layer was used to functionalize AuNPs on nanowire surface with higher surface coverage (Figure 7.4c) and the devices were termed as AuNPs functionalized In_2O_3 NW-FET (AuNPs F-NW-FET). The second type of devices were fabricated without using SAM layer where AuNPs solution was directly added to the In_2O_3 nanowire solution and a low surface coverage of AuNPs was observed (Figure 7.4d) due to physical adsorption, these devices were termed as AuNPs decorated In_2O_3 NW-FET (AuNPs D-NW-FET). Figure 7.5 shows the TEM images for different Au loading time using APhS-SAM layer.

Figure 7.6(a) shows the I_d - V_d characteristics at different gate voltage (V_g) for the AuNPs F-NW-FET. Non-linear and asymmetrical characteristics indicate Schottky nature of the metal-semiconductor (MS) junction with large resistance of $290 \text{ M}\Omega$ at $V_g = -5 \text{ V}$. A threshold voltage of -8.5 V with a large sub threshold swing ($\sim 1 \text{ V/decade}$) at a fixed V_d of 2 V was obtained from the I_d - V_g plot for the same device, shown in Figure 7.6(b). Similar Schottky behavior was obtained for devices of AuNPs D-NW-FET and samples without AuNPs. A larger threshold voltage of -13.6 V with a smaller threshold voltage swing of $\sim 185 \text{ mV/decade}$ was previously found for Ohmic contacts using the same nanowires (chapter 6).

Figure 7.6 Transfer characteristics of a single nanowire FET, (a) I_d - V_d curves showing Schottky type of device characteristics, (b) I_d - V_g characteristics at a drain voltage of 2 V.

To understand the effect of AuNPs coverage on nanowire surface, both devices were tested for the detection of pollutant gas carbon monoxide (CO) at room temperature. Drain voltage (V_d) was kept constant at 2 V and gate voltage (V_g) was kept at -5 V (within the threshold region of the F-NW-FET) during all the measurements. The sensing response of the bare single In_2O_3 Schottky device (without using AuNPs) is described in chapter 6, where it has been observed that Schottky type devices exhibit better sensing responses towards CO gas in comparison to their Ohmic counterpart due to Schottky barrier height (SBH) modulation during CO gas exposure. Sensor response of the AuNPs F-NW-FET for 0.2-5 ppm CO gas is shown in Figure 7.7(a). A sensor response (S) of nearly 104 was obtained using AuNPs F-NW-FET towards 5 ppm CO gas with a response time of ~130 s and recovery time of ~50 s (Figure 7.7a). We were able to detect distinct electrical changes for the CO gas concentration down to 0.2 ppm using AuNPs F-NW-FET at room temperature. Figure 7.7(b) shows the

sensitivity plot for the CO gas at room temperature under 50 % RH. A decreasing slope with increasing concentration of CO gas indicates saturation in response towards higher gas concentration (Figure 7.7b). A lower sensor response of ~ 4.5 with a shorter response and recovery times of 17 s and 12 s respectively, was obtained for 5 ppm CO gas exposure (Figure 7.7c) using AuNPs D-NW-FET. The significant improvement in sensor response for AuNPs F-NW-FET is almost 23 times (Figure 7.7a) higher than the AuNPs D-NW-FET and almost 30 times better than bare nanowire sensor ($S = 3.5$, for 5 ppm CO using SCD) (chapter 6). The larger time constants (response and recovery time) for AuNPs F-NW-FET are attributed to the slow electronic transport through APhS-SAM layer. To confirm the role of AuNPs coverage in AuNPs F-NW-FET devices, we have used nanowires with different Au loading time (e.g. 10 min, 20 min, 30 min and 60 min) as shown in Figure 7.5.

Figure 7.7 Gas testing plots for sensor operated at room temperature; (a) response plot for the AuNPs F-NW-FET (standard 60 min loading time), when exposed to 5 – 0.2 ppm CO and inset shows a zoomed view of the I_d -time plot for 5 ppm CO gas, (b) sensor response plot for CO gas at room temperature for the same device as shown in the inset. The drain and gate voltages were kept constant at $V_d = 2$ V and $V_g = -5$ V respectively, during sensing experiment, (c) Sensor response towards 5 ppm CO gas in different cycles using a AuNPs D-NW-FET device and (d) shows the sensor response towards 5 ppm CO gas from the AuNPs F-NW-FET device for 10 min Au loading time.

Nanowires showed a lower AuNPs coverage for 10 min and 20 min. The device with 10 min Au loading was tested for 5 ppm CO gas under similar operating conditions and a sensor response of ~23.5 was obtained as shown in Figure 7.7(d). The lower sensor response (in comparison of ~104 of 60 min Au loading device) evidently shows the importance of high loading of metal nanoparticles. The comparison of sensor responses from different devices is shown in Figure 7.8. It is noteworthy that the nanowires coated with only APhS SAM did not improve the sensor response, corroborating our findings on the role of metal nanoparticles.

Figure 7.8 Sensor response comparison for 5 ppm CO gas obtained from; OCD (Ohmic contacted device), SCD (Schottky contacted device), AuNPs D-NW-FET, nanowire coated with only APhS SAM, AuNPs F-NW-FET for 10 min and 60 min Au loading respectively.

7.3.1 Sensing Mechanism

Oxygen chemisorption on the MO_x nanowires plays a crucial role in the CO oxidation and hence electrical transport properties.^{165, 169} The chemisorption of oxygen species depends strongly on temperature and the surface characteristics of the nanowire material.^{236, 237} A room temperature thin film sensor shows weak sensor response mainly due to the existence of large number of grain boundaries in the polycrystalline film which provides large energy barriers on the electrons percolation path. This necessitates the need of thermal activation to improve gas adsorption/desorption. In contrast, sensor response at room temperature can be found in single nanowire sensors mainly due to the single crystalline nature providing better conductivity and reduced energy barriers for the current injection across the device with the assistance of gate control. In the nanowire transistor configuration, the electric field applied at the gate electrode modulates the carrier concentration, which in turn significantly affects adsorption and desorption behaviors of gas molecules or gas sensitivity.¹⁹⁰

The presence of high work function metal nanoparticles on the surface of n-type semiconducting nanowire leads to nanoscopic depletion region (nano-Schottky barriers, due to difference in work function) at MS interface, which modulates the device conductance.^{226, 220, 227} The depletion region around nanoparticle improves the sensor response due to the nano-Schottky barriers modulation during CO gas exposure (Figure 7.9). In addition, a well known “spillover effect” has to be taken into account, where metal nanoparticles catalytically activate the dissociation of molecular species, and finally the atomic products diffuse to the MO_x support.^{224-226, 220, 227} The size of the spillover zone depends on the particle size and experimental conditions.²³⁸ At higher particle coverage, the spillover zones essentially cover

most of the nanowire surface in F-NW-FET which increase the CO oxidation into CO₂ due to the availability of increased chemisorbed gas ions. We have observed that sensor response dramatically depends on the metal nanoparticle coverage on the nanowire surface which corroborates with the previous results.²²⁰ High coverage of the AuNPs on the nanowire surface has been tailored with the use of APhS-SAM layer in this work. The sensing mechanism of such devices can be explained in the following steps; first is the effect of higher AuNPs coverage on nanowire, secondly the role of SAM layer on sensing enhancement and electronic transport through it and finally SBH modulation in a Schottky device during gas exposure.

Immobilization of AuNPs facilitates adsorption of gaseous species on the nanoparticle surfaces at room temperature due to the higher surface defects available in nanoparticles surface, highly conductive nature and availability of free electrons in gold.^{209, 213, 239, 240} In this work, by using the fact that gold is a good catalyst for the CO oxidation,^{239, 240} the high density of AuNPs attached to the nanowire increases the CO oxidation into CO₂ which reflects as an increased conductance of the nanowire-channel. In the present Au-In₂O₃ nanowires system, the conductance changes during the CO gas exposure is due to the exchange of electrons between chemisorbed species and Au decorated In₂O₃ nanowires. Higher surface coverage by AuNPs increases the CO oxidation in to CO₂ via catalytic activation. In contrast, a smaller sensor response of 4.5 (for AuNPs D-NW-FET) was obtained compare to the sensor response of 3.5 for bare NW-FET in chapter 6. The small enhancement in sensor response of AuNPs D-NW-FET devices can be attributed to the low AuNPs coverage as shown in the TEM images (Figure 7.4d). It is well documented that gold particle sizes influence the CO oxidation. The increasing catalytic oxidation on smaller metal

particle size is mainly due to the availability of higher density of reactive defect sites (edge, kink, or step sites).²⁴¹ However, it has been observed that the particle size dependence CO oxidation is much influenced by the support material.^{242-244, 223, 218} For inert support materials (*e.g.* Au/SiO₂, Au/Al₂O₃), the critical particle diameter is reported around 2 nm.^{223, 218} For active support materials (*e.g.* Au/Fe₂O₃, Au/TiO₂), the gold particle size plays secondary role.^{242, 218} Catalysis with Au particles as large as 12 nm (Au/Fe₂O₃) or 30 nm (Au/TiO₂) was able to show comparable catalytic effects to those used with smaller Au particle sizes.²¹⁸

Figure 7.9 Illustration of, (a) band diagram of the metal-SAM-semiconductor system, (b) schematic of the AuNPs F-NW-FET device, showing the formation of depletion regions (white color) underneath the AuNPs.

The primary role of the APhS-SAM layer is to increase the density of the AuNPs on the nanowire surface which can be clearly seen in TEM image (Figure 7.4c). Presence of SAM layer can affect the volume of the depletion region underneath nanoparticle, as transportation of electrons between nanowire and nanoparticle through APhS-SAM molecule would not be as fast as that without APhS-SAM. Studies have shown that the electronic transport through SAM layers could be in the form of tunneling, thermionic or hopping.²⁴⁵

The carrier transport is reported to be dominated by tunneling when the Fermi levels of metal falls within the HOMO–LUMO gap of the SAM.²⁴⁶ We have estimated a HOMO-LUMO gap of ~5.633 eV for the APhS-SAM (thickness ~ 1 nm) using Gaussian simulation. It is well known that polar SAMs (e.g. APhS-SAM) alter the electronic properties at their interfaces with metals/semiconductors by adjusting the surface potential,^{247, 248} carrier density,^{249, 250} electron affinity,^{251, 252} and work function.^{253, 254} A net electrical dipole perpendicular to the surface/interface is introduced by polar monolayer.^{247, 255} Accordingly a potential shift at the interface takes place which tune the work function and electron affinity at a surface. Thus changes the band offset and band bending. As a result, the Au/SAM interface behaves as an active support system where the size of Au particles plays secondary role. Due to the slower electronic transport through APhS-SAM layer, F-NW-FET shows a larger response and recovery time (130 s and 50 s respectively) in comparison to D-NW-FET (17 s and 12 s for 5 ppm CO gas).

In a single NW-FET, the presence of potential barrier at the MS interface plays a crucial role in the charge transportation across the interface.²²⁸⁻²³⁰ The increased conductance (as seen in Figure 7.7(a) inset) of the channel has another advantage; due to the large change in the relative conductance of the nanowire channel, lowering of SBH takes place at the MS interface and a large change in the relative current (100 nA to ~ 8 μ A for 5 ppm CO gas in 300 seconds shown in the inset of Figure 7.7a) was observed when the device was operated under forward bias of 2 V. In such devices, potential barriers are present at the two ends of the nanowire and these are connected in series with the nanowire channel resistance; as a result the device shows a large resistance initially. By using the AuNPs functionalization to the nanowire channel, all three resistances in series are decreased due to the transfer of

electrons from the CO molecules to the nanowire channel which results in lowering of the net resistance of the device. As a result of the drastic decrease in net resistance of the device, a large relative change in the device conductivity was resulted. The significant enhancement in the sensor response at room temperature is mainly attributed to the higher AuNPs density at the nanowire surface. The Schottky barrier in this study has been controlled mainly by the contact material properties.

7.4 Summary

In summary, a highly sensitive device for the CO gas sensing at room temperature has been demonstrated by combining the Schottky contact effect with a metal nanoparticle functionalized nanowire channel. APhS-SAM modification of In_2O_3 nanowires with amine terminated groups resulted in a high coverage of AuNPs attached on the nanowire surface. In addition to the high density of AuNPs on the NW surface, the utilization of the Schottky contact at the nanowire-electrode junction plays a crucial role in the sensor response. The modulation of SBH due to the higher number of electrons transferred to the nanowire channel during CO oxidation, made the device highly sensitive towards CO gas, which is found to be depending on the degree of coverage of the AuNPs on the In_2O_3 nanowire surface. The comparative sensing performances of single nanowires after surface functionalization with Au catalyst nanoparticles show significant improvement in sensor response towards reducing gas like CO.

Chapter 8

Conclusions and Future Recommendations

8.1 Conclusions

Controlled growth of In_2O_3 nanostructures was established in a VLS horizontal furnace growth. Single crystalline, cubic In_2O_3 nanowires, nanotowers and long layered nanorods were successfully synthesized on Si/alumina substrates by varying source temperature using Au as catalyst. Other nanostructures such as; rectangular cross sectional nanorods, dendritic nanostructures, In_2O_3 -ZnO core-shell nanowire and hierarchical nanostructures were synthesized by varying the growth parameters. Growth temperature was found to play a crucial role in defining the morphology under confined conditions. The diameter and morphology of the growing structures were altered by tuning the growth temperature under confined conditions of the In vapors. Nanotowers with truncated octahedrons along the length were synthesized as a result of VS - VLS alternative growth. The confinement of indium vapors provides higher indium vapor saturation which serves to initiate lateral growth. Optical characterizations on the as grown In_2O_3 nanostructures show the oxygen deficient nature of the as grown nanostructures which is essential for the sensing application. In the In_2O_3 -ZnO core-shell nanowire, ZnO shell was in polycrystalline form due to the random nucleation of the ZnO on In_2O_3 nanowire's surface at low growth temperature and short growth duration.

The resistor based devices fabricated on as grown nanowires alumina substrate were first tested for various pollutant gases. Grainy outer shell layer was observed to increase the adsorption of gaseous species which play a vital role in the enhanced sensor response for pollutant gases. A combination of homo- and hetero-interfaces formed at the junctions in the core-shell nanowires sensor is the reason for the improved sensitivity toward reducing gases compared with the sensor based on the nanowires without a shell layer. However, pure In_2O_3 nanowires were observed to show a better response towards NO_2 (oxidizing gas). On the other hand, Zn- doping into the In_2O_3 nanowires has enhanced the sensor response for H_2 , ethanol and CO (reducing gases). Zn- In_2O_3 nanowires have shown ~5, 7 and 15 times enhanced sensor response for 400 ppm CO, 4000 ppm H_2 and 400 ppm ethanol respectively compared to pure In_2O_3 nanowires. Zn incorporation into the In_2O_3 lattice creates more oxygen vacancies and increases the surface defects which enhance the receptor function for reducing gases. NO_2 calibration curves on Zn- In_2O_3 nanowires at different RH indicate that the interactions of NO_2 molecules are dissociative towards higher relative humidity.

Resistor based nanowire network devices have shown low sensor response at lower temperature. It is very difficult to fabricate a resistor based nanowire network device which shows high sensor response at room temperature. We have developed a strategy to realize room temperature gas sensing using high quality nanowire channel in NW-FETs configuration. A NW-FET device with better transistor characteristics is always required to obtain a high sensor response. Zn- In_2O_3 NW-FET showed good transfer characteristics. The as-fabricated device showed excellent operating characteristics with a high drain current on/off modulation ratio of 10^6 , a high on-state current of 8×10^{-6} A at $V_d = 5$ V, a small sub-threshold gate voltage swing of 140 mV/decade and an electron mobility of $139 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Gas sensing properties of such sensor has been studied for 1-5 ppm CO gas at room temperature. An enhanced sensor response and a good selectivity over NO and NO₂ was correlated to the defects generated and the modification of the Fermi level position in a Zn-In₂O₃ NW due to the Zn-doping.

To enhance the sensor response at room temperature, we have studied the effect of channel and contact resistance on sensor response. Utilization of contact resistance has been demonstrated as an effective way to improve the sensor response for two different classes of gas at room temperature. We have fabricated SCD and OCD by tuning the contact metal and nanowire contact resistance. These two different types of devices have been found useful for two different classes of gases; OCD exhibited large response for the oxidizing gases (e.g. NO) and SCD devices showed better response for reducing gases. In OCD, main contribution to sensor response comes from the nanowire channel while the modulation of SBH dominates in the SCD. Achieving high sensor response by controlling the contact behavior at the MS interface suggests the possibility of deploying these devices at room temperature for a particular class of gases with distinct response. This work delineates the importance of device type selection for a particular class of gas with higher response.

Finally, a highly sensitive device for the CO gas detection was fabricated using catalytic oxidation of CO on Au nanoparticles. A SAM layer was used to improve the Au-NPs coverage on nanowire surface. The nanoparticle functionalized nanowire was then used as a channel in a SCD. The modulation of SBH due to the higher number of electrons transferred to the nanowire channel during CO oxidation, made the device highly sensitive towards CO gas. This was found to be depending on the degree of coverage of the AuNPs on the In₂O₃ nanowire surface. The comparative sensing performances of single nanowires after surface

decoration with Au catalyst nanoparticles showed significant improvement in sensitivity towards reducing gas like CO.

This work represents the MOx nanowires as a powerful detection platform for chemical sensing at room temperature. These NW-FET devices have a number of key features including high sensitivity, better selectivity, low power consumption, and potential for integration of addressable arrays in electronic nose technology (an electronic nose is a smart device that is designed to detect and discriminate among complex odors using arrays of sensors).²⁵⁶ The application of gate potential in NW-FETs can be used to improve the sensitivity and electrically desorb the adsorbed gas molecules. Such nano-sensor devices have advantages over the resistor based two terminal devices where a high temperature is needed to desorb the gas molecule. In the literature, one of the most sensitive CO gas sensor was fabricated by *Aruna et al.*⁸⁴ In that work, they have claimed to detect 10 ppb CO gas ($S = 6.5$) at an operating temperature of 640 K on a SnOx-Pd nanoparticle based resistive sensor. In comparison, we are able to detect 200 ppb CO gas ($S = 10$) at room temperature on AuNP-F-NW-FET (chapter 7), which is the best performance at room temperature till date. These findings indicate that single NW-FET based sensor devices are highly promising candidates for future smart chemical sensing.

8.2 Future Recommendations

Room temperature chemical sensing using single NW-FET has attracted immense research attention due to its low operating temperature and highly sensitive nature. In this project, two different types of NW-FET devices; Ohmic and Schottky contacted devices have been tested

at room temperature gas sensing. Further, devices with high gold nanoparticles loading using APhS SAM layer was used for the enhanced CO detection at room temperature. Overall a highly sensitive device for CO gas was fabricated. In spite of the highly sensitive devices there are still some drawbacks, leaving room for future improvements.

8.2.1 Improvements on single nanowire alignment: The nanowire integration into nano-devices to explore their nano-electronic properties is a significant challenge. In this project, we have aligned single nanowires using DEP method, which is very efficient method for nanowire alignment.^{257, 96} In this work, more efforts were focused to explore sensing mechanism and accordingly improve the sensitivity of the device for a particular class of gas. It is important to have an efficient method to precisely maneuver and align individual nanowires in order to have larger mass production. We have explored variables including frequency and voltage applied on their effects on nanowire alignment. The nanowire alignment also depends on the electrode geometry, inter-electrode gap, thickness of the electrode tip, etc. So a single nanowire manipulation system to precisely maneuver and align individual nanowires is much desirable. Devices optimized with electrode geometry and inter electrode gaps for single nanowire alignment can improve the yield of single NW-FET fabrication.

One alternative approach can be proposed using pre-aligned nanowires on nanopatterned substrate. A substrate with nanopatterned resist can be used to accommodate a single nanowire. Then in the subsequent steps, resist can be removed or patterned for contact formation. The schematic illustration of the procedure to align is shown in Figure 8.1. Step 1 depicts a substrate coated with resist. Step 2 shows the nanopatterns generated on resist for the accommodation of the single nanowire. This step is critical as it decides the size of the

pattern to accommodate only single nanowire. Step 3 shows nanowires in the patterned slots by dropping nanowire solution on the patterned substrate. In the step 4 resist is removed, which left behind the aligned nanowires ready to be contacted.

Figure 8.1 Schematic illustration of the proposed nanowire alignment method.

8.2.2 Improvements on selectivity: Selective high sensor response at room temperature towards a particular gas has been a challenging issue for the researchers of this community. In this project we have fabricated a highly sensitive CO gas sensor. Zn-In₂O₃ nanowires have shown better sensitivity towards CO compared to NO_x gases at room temperature. Similar sensors can be fabricated for selective detection of other gases using other dopants/catalyst or probes. All such single nanowire based devices can be integrated on a multiplexer (e.g. electronic nose) to have a selective sensor response at room temperature.

8.2.3 Sensing mechanism: In many instances, the reason of improving sensor response is not well understood. For example, the role of dopant is not clearly understood,

especially when the dopant amount is very low. More efforts in the understanding of sensing mechanism can help to optimize the sensor response. In-situ spectroscopic techniques (where structural changes after doping can be precisely monitored) can help to understand more on the dopant role in enhancing sensor response. Schottky contact devices have shown improved sensor responses especially for reducing gases, the sensing mechanism is well accepted as the modulation of Schottky barriers height during gas exposure. Different Schottky barriers heights can be useful to study the optimization of the sensor response. The barrier heights can be tuned by using different contact metals with different work functions.

8.2.4 Multiple nanowire sensor devices: Multiple nanowire channels can alter the sensor response. The multiple nanowires present in the channel can affect the sensor response in both ways. As it is known that the NW-FET based sensor devices show optimum sensor response when operated at threshold region. When the device is made of single NW, it is easier to operate the device in the optimized conditions. On the other side, if the device is made of multiple nanowires, it can be more sensitive provided that all the nanowires are operated in the threshold regions (optimized conditions). Such devices are difficult to fabricate where all nanowires work at the similar threshold conditions. If majority of the nanowires in multiple nanowire FET device do not work in the threshold region during operation, it may worsen the device performance. As the sensor response depends on the relative change in the conductance before and after gas exposure, nanowires operating in “saturation” or in “off” state show minimal change in conductance. This tends to deteriorate the sensor performance. To fabricate ultrahigh sensitive devices using multiple nanowires, it is important and necessary to operate all nanowires in the threshold region. Presence of multiple nanowires can improve the reliability and life time of the sensor.

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List of Publications

Journal Papers:

1. “Temperature-controlled growth of In_2O_3 nanowires, nanotowers and ultra-long layered nanorods” by **Nandan Singh**, Tao Zhang and Pooi See Lee* Nanotechnology 20(2009)195605.
2. “Room temperature CO gas sensing using Zn-doped In_2O_3 single nanowire field effect transistors” by **Nandan Singh**, Chaoyi Yan, Pooi See Lee; Sensors and Actuators B 150 (2010) 19.
3. “Sensing Properties of Different Classes of Gases Based on the Nanowire-Electrode Junction barrier modulation” by **Nandan Singh**, Yan Chaoyi, Lee Pooi See, Elisabetta Comini; Nanoscale 3, (2011), 1760.
4. “Gold Nanoparticles Functionalized In_2O_3 Nanowires as CO Gas Sensors with a Significant Enhancement in Response” by **Nandan Singh**, Raju Kumar Gupta, Pooi See Lee; ACS Appl. Mater. Interfaces, 3 (7), (2011), 2246.
5. “Synthesis of In_2O_3 -ZnO core-shell nanowires and their application in the gas sensing” by **Nandan Singh**, Andrea Ponzoni, Raju Kumar Gupta, Pooi See Lee and Elisabetta Comini; Sensors and Actuators B (accepted).
6. “Chemical sensing investigations on Zn- In_2O_3 nanowires” by **Nandan Singh**, Andrea Ponzoni, Elisabetta Comini and Pooi See Lee. Sensors and Actuators B (Accepted).
7. “Morphology Control of Indium Germanate Nanowires, Nanoribbons and Hierarchical Nanostructures” by Yan, Chaoyi; **Singh, Nandan**; Lee, Pooi See; Crystal Growth & Design 9, (2009), 3697.
8. “Wide-band gap Zn_2GeO_4 nanowire networks as efficient ultraviolet photo detectors with fast response and recovery time” by C. Y. Yan, **N. Singh**, P. S. Lee, Appl. Phys. Lett. 96(5), (2010), 053108.

9. “Kinking-Induced Structural Evolution of Metal Oxide Nanowires into Single-Crystalline Nanorings” Chaoyi Yan, **Nandan Singh**, and Pooi See Lee; ACS Nano 4 (9) (2010) 5350–5356.
10. “Network-Enhanced Photo response Time of Ge Nanowire Photo detectors” by Chaoyi Yan, **Nandan Singh**, Hui Cai, Chee Lip Gan and Pooi See Lee; ACS Appl. Mater. Interfaces, 2(7), (2010), 1794–1797.

Conference Papers:

1. “Ultra-long Indium Oxide (In_2O_3) layered nanorods for NO_x sensing application” by **Nandan Singh** and Pooi See Lee. ICMAT Singapore 2009.
2. “Au decorated In_2O_3 nanowire field effect transistors for CO sensing at room temperature”, by **N. Singh**, P. S. Lee, E-MRS Spring Meeting, June 2010, Strasbourg, France.

Appendix

S1. Sensor response for NO_2 gas obtained from (a) pure In_2O_3 and (b) In_2O_3 -ZnO nanowires.

S2- I_d - V_g characteristic of the OCD at a constant V_d of 0.5 V.

S3. The resistance of undoped and Zn-In₂O₃ NW- FET, measured at $V_g = 0$ V.