HIGHLY SENSITIVE AND SELECTIVE CHEMICAL/GAS SENSORS USING HYBRID NANOWIRE-NANOCLUSTER BASED DEVICES

by

Geetha S. Aluri A Dissertation Submitted to the Graduate Faculty of George Mason University In Partial fulfillment of The Requirements for the Degree of Doctor of Philosophy Electrical and Computer Engineering



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Summer Semester 2012 George Mason University Fairfax, VA

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By

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Dedication

I dedicate this dissertation to my parents, Naga Durga Aluri and Venu Gopala Krishna Rao Aluri, for their love, endless support and encouragement.

Acknowledgments

During the course of this thesis, I was surrounded by a great team of supervisors, mentors and colleagues. Above all, I want to thank my supervisor, Dr. Rao Mulpuri, who instilled in me the courage and confidence to take on and lead this research effort. His encouragement and support gave me the positive energy to work in the right direction. I feel extremely fortunate to have worked with the finest advisors that one could possibly hope for.

I would like to thank Dr. Abhishek Motayed, who helped me through the last four years with sound and practical advice at all times, especially when the tasks seemed overwhelming and never-ending. I would like to express my gratitude to Dr. Albert Davydov for his highly valued advice, constructive questions and suggestions about the research project. I benefited greatly from useful discussions with Dr. Sergey Krylyuk, Dr. Vladimir P. Oleshko and Dr. Ritu Bajpai in many technical matters.

I am short of words to express my deepest gratitude to my family and friends, whose continuous love, sacrifice, support and encouragement have allowed me to pursue my ambitions.

Finally, I want to acknowledge that this research was funded by the National Science Foundation, under the GOALI research grant ECCS-0901712. The nanowire devices were fabricated at the Nanofab clean room of the NIST Center for Nanoscale Science and Technology.

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List of Abbreviations

ADF	annular dark-field
AFM	atomic force microscopy
BF	bright-field
BOE	buffered oxide etch
BTEX	benzene, toluene, ethylbenzene, xylene
CVD	chemical vapor deposition
DIP	dual in-line package
DI	deionized
EBSD	electron backscatter diffraction
FET	field effect transistor
FFT	fast fourier transform
GADDS	general area detector diffraction system
GaN	Gallium Nitride
HAADF	high-angle annular dark-field
HR-ATEM	high resolution analytical transmission electron microscopy
HR-TEM	high resolution transmission electron microscopy
IR	Infrared
MBE	molecular beam epitaxy
MFC	mass flow controller
МО	metal oxide
NC	nanocluster
NP	nanoparticle

NW	nanowire
NWNC	nanowire-nanocluster
ppb	parts per billion
ррт	parts per million
ppt	parts per trillion
RIE	reactive ion etch
rpm	revolutions per minute
RTA	rapid thermal anneal
SAED	selected area electron diffraction
sccm	standard cubic centimeter per minute
SEM	scanning electron microscope
slpm	standard liter per minute
\mathbf{SnO}_2	Tin oxide
STEM	Scanning Transmission Electron Microscopy
ТЕМ	transmission electron microscopy
TiN	Titanium nitride
TiO_2	Titanium dioxide
UV	Ultra violet
VOC	volatile organic compound
WZ	Wurtzite
XRD	X-ray diffraction
ZnO	Zinc oxide

Abstract

HIGHLY SENSITIVE AND SELECTIVE CHEMICAL/GAS SENSORS USING HYBRID NANOWIRE AND NANOCLUSTER BASED DEVICES

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George Mason University, 2012

Dissertation Director: Dr. Mulpuri V. Rao

The development of reliable, portable gas sensors that can detect harmful gases in real-time with high sensitivity and selectivity, is very important for clean environment and national security. In the last few decades, significant advances have been made in the field of metal oxide based thin-film sensors. Metal oxide sensors have been utilized for several decades for low-cost detection of combustible and toxic gases. However, issues with sensitivity, selectivity, and stability have limited their use, often in favor of more expensive approaches such as IR sensors and gas chromatography. In recent years, there has been a tremendous interest in the development of nano-engineered materials, such as nanowires and nanoclusters, for gas sensing because of their high sensitivity. In most of these nanostructure based sensors, poor selectivity and limited sensitivity are still major obstacles for their commercialization. For real-world applications, selectivity between different classes of compounds (such as between aromatic compounds and alcohols) is highly desirable. In fact, an ideal chemical sensor is one that can distinguish between the individual analytes belonging to a particular class of compounds, e.g. detection of the presence of benzene or toluene in the presence of other aromatic compounds. This is extremely challenging as most semiconductor-based sensors use metal-oxides (such as SnO_2 , In_2O_3 , ZnO) as the active elements, which have inherent non-selective surface adsorption sites.

Recently, a new class of nanowire-based gas sensors have gained interest. The nanowire-nanocluster (NWNC)-based gas sensors represent a way of functionalizing the surfaces of nanowires for selective adsorption and detection of analytes. They also offer the potential of tuning their sensitivity and selectivity by adjusting the composition, size, and density of the nanoparticles which decorate the nanowires. This makes them a good alternative to conventional metal-oxide based thin film sensors. In recent years, researchers have demonstrated the potential of NWNC hybrids for sensing many different chemicals. However, most of the hybrid devices developed so far require elevated working temperatures, have long response/recovery times, and operate in inert atmospheres, which limit their use in environmental, domestic, and industrial applications.

Approach of this work utilizes n-type (Si doped) GaN nanowires functionalized with different metal oxide and metal-metal oxide composite nanoclusters for highly selective gas sensing. In this work, it has been demonstrated that the GaN-TiO₂ (nanowire-nanocluster) hybrid devices use the photocatalytic properties of TiO₂ to sense specific volatile organic compounds mixed in air at room temperature and ambient humidity. The photo-modulated GaN/TiO₂ NWNC hybrids showed remarkable selectivity to benzene and related aromatic compounds, with no measureable response for other analytes (like alcohols, ketones, aldehydes, amides etc) at room temperature. Xylene, ethybenzene, benzene, and toluene were detected at concentration levels of 50 ppb in approximately 75 s. These sensor devices were highly stable and able to sense aromatic compounds reliably with concentrations as high as few percents in air. These GaN/TiO_2 NWNC hybrids also sensed very low concentrations of explosive nitro-aromatic compounds as well. The hybrid sensor devices were able to detect trinitrotoluene (TNT) concentrations as low as 500 ppt in air and dinitrobenzene concentrations as low as 10 ppb in air in approximately 30 s.

It was found that sensors with TiO₂-Pt multicomponent NCs on GaN NW were only sensitive to methanol, ethanol, and hydrogen. Higher carbon-containing alcohols (such as n-propanol, iso-propanol, n-butanol) did not produce any sensor response. The GaN/(TiO₂-Pt) hybrids were able to detect ethanol and methanol concentrations as low as 100 ppb in air in approximately 100 s, and hydrogen concentrations from 1 ppm to 1% in nitrogen in less than 60 s. These sensors have the highest sensitivity towards hydrogen. Prior to the Pt deposition, the GaN/TiO₂ NWNC hybrids did not exhibit any response to alcohols. The GaN/Pt hybrids only showed sensitivity to hydrogen and not to methanol or ethanol. The sensitivity of GaN/Pt hybrids towards hydrogen was lower compared to the GaN/(TiO₂-Pt) hybrids. GaN/SnO₂ NWNC prototype devices were also developed in this study, which showed selective response to alcohols for a wide range of alcohol vapor concentrations, from 5000 ppm down to 1 ppm in air. It is observed that the sensor response decreases with the increasing carbon chain from methanol to n-butanol.

This study indicates the potential of multicomponent NWNC based sensors for developing the next-generation of ultra sensitive and highly selective chemical sensors. Through combinations of metal and metal-oxides available, one can produce a library of sensors, each with precisely tuned selectivity, on a single chip for detecting a wide variety of analytes in many different environments at room temperature. Also, due to the small magnitude of device operating current and sensor activation at low illumination intensity, these sensors have low power consumption which makes them suitable for portable applications.

Chapter 1: -Introduction

A chemical sensor is a device that identifies a chemical species and quantifies the concentration of atoms, molecules, or ions in gases or liquids by producing a measurable signal [2]. A typical sensing system can be used to detect harmful gases and interface with a control system to transmit warnings via a series of audible and visible signals such as alarms and flashing lights, when dangerous levels of gases are detected.

1.1 Importance of chemical/gas sensors

Detection of chemical species in air such as industrial pollutants, poisonous gases, chemical fumes, and volatile organic compounds (VOCs) is vital for the health and safety of communities around the world [3]. Chemical and explosive detection systems constitute the first line of defense against chemical weapons and terrorist threats [4]. Gas sensors are vital in commercial and industrial applications like combustion engine monitoring, process control, and environmental monitoring [5]. Chemical/gas sensors also find applications in food quality control, breath analysis and disease detection. It is because of these important applications, extensive research is being done on gas sensors and the advent of nanotechnology is continually influencing the modern sensing systems in view of making sensors cheaper with higher performance characteristics.

1.2 Characteristics of a chemical sensor

A sensors performance can be characterized by the following set of important parameters.

- Sensitivity: is the change of measured signal per analyte concentration unit change in input, i.e., the slope of a calibration graph.
- Selectivity: is a sensor's ability to discriminate between the components of a gas mixture and provide detection signal for the component of interest.
- Stability: is the ability of a sensor to provide reproducible results for a certain period of time. This includes retaining the sensitivity, selectivity, response, and recovery time.
- Detection limit: is the lowest concentration of the analyte that can be detected by the sensor under given conditions, particularly at a given temperature.
- Dynamic range: is the analyte concentration range between the detection limit and the highest limiting concentration.
- Resolution: is the lowest concentration difference that can be distinguished by sensor.
- Response time: is the time required for sensor to respond to a step concentration change from zero to a certain concentration value.
- Recovery time: is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.
- Working temperature: is usually the temperature at which the sensor operates.

An ideal chemical sensor should be able to operate at room temperature and possess high sensitivity, good selectivity, high stability, low detection limit, a wide dynamic range, good resolution, fast response and recovery times.

1.3 Current sensor technologies and their limitations

Due to the expansive volume of the literature available on novel sensing techniques, only portable gas sensing technologies are covered here.

- 1. Catalytic sensors: Commonly called a pellistor, a heated wire is used to detect flammable, combustible gases via catalytic oxidation [6]. As, the gas comes into contact with the catalytic surface, it is oxidized releasing heat. The electrical resistance of the wire changes and is measured by an electrical "Wheatstone Bridge" circuit, which accurately records this change. This change is then converted into a readable display on the instrument. The catalytic combustion sensors typically use a lot of power to operate, has interference issues and regularly requires fresh or recharged batteries for the instrument. These sensors require oxygen or air to work and they are positioning critical [7].
- 2. Electrochemical sensors: Electrochemical sensors are typically available for a variety of toxic gases like carbon monoxide, nitrogen oxides and chlorine. The target gas diffuses into the membrane at the top of the sensor and then reacts with the chemicals on the sensing electrode to generate an electrical current [8]. This electron flow can be measured and displayed. Cross-sensitivity to alcohol vapors and unsaturated hydrocarbons is the common problem. Short shelf life and limited sensing range (works in relatively low concentrations) are the other disadvantages of these sensors.

- 3. Infrared sensors (IR sensors): IR sensors work via a system of transmitters and receivers commonly used to detect combustible gases, specifically hydrocarbon vapors and carbon dioxide. Typically, the transmitters are light sources and receivers are light detectors. If a gas is present in the optical path, it will interfere with the power of the light transmission between the transmitter and receiver. The altered state of light determines the type of gases present and the amount of gas is determined by how much light the gas absorbs [9]. The main drawback to IR sensors is their cost. IR sensors are more complex and expensive. They are not suitable for use in smaller areas as well.
- 4. Photoionization detectors (PIDs): PIDs are mainly used to detect volatile organic compounds. Photoionization detectors rely on specific chemical properties of the VOCs. Instead of absorbing light, a PID uses a UV light source to ionize electrons off gas molecules. Once the gas is ionized, it passes through two charged plates, which separate the gas ions and the free electrons. As the gas ions flow towards the plates, a current is generated between the two plates. The greater the concentration of the component, the more ions are produced, and the greater the current [10]. The current is amplified and displayed on an ammeter. PID sensors are not at all specific, they will indicate that some VOCs are present, but not what type. They are non-specific, expensive, complex and require frequent maintenance.
- 5. Metal oxide thin film sensors: They are used for detecting a range of gases including toxics and combustibles and work via a gas sensitive film that is composed of tin or tungsten oxides [11]. Materials are held at temperatures in the range 300-500 °C where useful reactions proceed at sufficient rate. The detection principle of resistive sensors is based on change of the resistance of

a thin film upon adsorption of the gas molecules on the surface of a semiconductor. The gas-solid interactions affect the resistance of the film because of the density of electronic species in the film[12]. More detail on this important class of sensors will be given in chapter 2. Unfortunately, resistive metal-oxide gas sensors have serious drawbacks in terms of selectivity, long-term baseline drift, and high-temperatures required for operation, which limits their use in demanding applications.

6. Field effect sensors: These sensor devices can be used for detecting toxics, explosives and VOC's. The MOSFET sensor device is based on a field effect transistor with a catalytic metal as the gate contact. The gate voltage controls the current through the MOSFET device. The gas molecules affect the voltage to the gate contact thereby changing the current through the transistor [13]. For the MOSFET sensor, gate and drain are connected and the sensor operates as a two-terminal device. The gas response is recorded as a voltage change in the sensor signal. These sensors have low-sensitivity and limited selectivity. The metal gates in these FETs have to be thin and porous to achieve the required sensitivity, which introduces serious reliability issues for demanding applications.

Table 1.1 summarizes the applications and the limitations of the technologies discussed above.

1.4 Strategy for developing high performance sensor devices

It is well known that due to their high surface to volume ratio, the electrical and physical properties of nanoparticles (NPs) and nanowires (NWs) nanowires change significantly in response to their environments [14–16]. In case of nanoparticles,

Type of devices	Applications	Limitations
Catalytic gas sensors	Flammable and Explosive Gases	Heated, Interference
Electro-Chemical Detectors	Toxic Gases in Portable Systems	Short operating life-time, Non-selective, Expensive
Photo-Ionization Detectors	Volatile Organic Compounds (VOCs)	Macroscale, Short-shelf life, Cross-sensitivity, Limited working range
Infrared Sensors	Toxic Gases, Explo- sive Gases, Green- house gases	Big, Expensive, Requires lot of power and routine maintenance
Metal-Oxide Thin Film Sensors	Toxic Gases, VOC's, Explosive Gases	Reliability issue due to high temperature opera- tion, Cross-sensitivity
Field Effect sensors	Toxic Gases, VOC's, Explosive Gases	Limited sensitivity and se- lectivity

Table 1.1: Comparison of the current technologies for portable sensing systems.

direct electrical measurements of these changes are not feasible, which is often the fastest and most direct method to identify the reactions occurring at the surface. Nanowires, on the other hand, are well suited for direct measurement of changes in their electrical properties (e.g. conductance/resistance, impedance). There has been a vast amount of research demonstrating beyond doubt the enhanced sensitivity, reactivity, and catalytic efficiency of the nanoscale structures. Unfortunately, for the nanowires, the surface/adsorbate interactions are limited due to availability of one type of binding sites. Despite being highly sensitive, nanowires too will suffer from the lack of selectivity as their bulk-counterpart devices. A fundamental study based on the sensing properties of nanocluster-nanowire hybrid devices has been proposed in this work to mitigate this problem of selectivity. These nanoclusternanowire hybrid devices will be realized by placing nanoclusters of different metals and metal-oxides on Gallium Nitride nanowires. Nanoclusters of metals or metaloxides supported by Gallium Nitride (GaN) will act as nanocatalysts, which will not only increase the sensitivity and lower the detection time, but most importantly it will enable us to tailor the selectivity of these structures, by incorporating different nanocluster materials.

1.5 Contributions and accomplishments

Gallium nitride nanowires functionalized with titanium dioxide, platinum-titanium dioxide composites and tin oxide nanoparticles have been used to selectively detect different aromatic compounds, alcohol vapors, traces of explosives and hydrogen. The sensors have been fabricated by standard microfabrication techniques.

- Fabrication of single nanowire devices: Though there have been some demonstrations of nanowire-nanocluster hybrids, most of the studies are on mats of devices. Interpreting the results in such cases becomes quite complicated due to the inter-wire connections. Reliability in the operation along with reproducibility is also a major roadblock. Single nanowire devices are developed by using a technique called dielectrophoresis, for precise alignment. Understanding the sensing mechanism becomes straightforward in these kinds of sensor devices.
- 2. Independent control of sensing and transducing properties of the sensor device: The electrical properties of the sensor are governed by the GaN nanowires and the metal/ metal-oxide nanocluster coating on the GaN surface controls the sensor selectivity. GaN nanowire semiconductor backbone is found to be chemically inert to the analytes. Selectivity and sensitivity is determined by

the nanocluster material only ie., TiO_2 is found to be very selective to aromatic compounds and nitro-aromatic explosives. On the other hand Pt-TiO₂ composite clusters do not sense aromatics anymore and are highly sensitive to alcohols and hydrogen. SnO₂ clusters are highly selective to alcohol vapors.

- 3. Room temperature operation: Most of the conventional metal oxide sensors operate at high temperatures leading to reliability issues and demanding power requirements. Significant breakthrough of the demonstrated sensor devices is that they operate at room temperature in the ambient conditions, without the need of heating systems or vacuum evacuation. This implies that the developed technology has several advantages like low power operation, longer life times, wide choice of sensitive materials and ease of integration in a sensor system.
- 4. Photo-modulation of the sensing characteristics: The devices exhibit sensing behavior only in the presence of Ultra violet (UV) light. In other words, sensing action as enabled by UV light rather than high temperatures. A low-power light emitting diode (LED) can be used, which can be easily integrated into any system, ensuring longer lifetime and low power operation. The response of the devices to individual analytes can also be tuned by varying the intensity of light.
- 5. Fast response and recovery: The devices developed exhibited very fast response and recovery time i.e., in the order of 60 s to 80 s for most of the devices. The sensing action is very quick and it is repeatable without any downtime.
- 6. Wide sensing range and long lifetime: Most of the commercial technologies available can operate in a limited range only; either in high concentration

range (100 parts per million (ppm) to 20,000 ppm) or low concentration range (100 parts per trillion (ppt) to 10 ppm). The devices exhibit wide sensing range i.e., good sensitivity from concentrations as low as 500 ppt to concentrations as high as few percent (10,000 ppm). Even after prolonged usage, for over a year, most of the devices still operate well without any degradation in the sensing capabilities.

1.6 Organization of the dissertation

This dissertation has been presented in five chapters.

Chapter 1 (this chapter) gives a brief introduction to the reader about the importance of gas sensors in the day-to-day life. An overview of the current technologies for portable gas/chemical sensing and their major limitations are discussed. A strategy for developing high performance sensing devices has been introduced. Contributions and accomplishments of this work have been highlighted towards the end of the chapter.

Chapter 2 gives the background information and the motivation for the present study. Metal oxide sensors, which have been widely used for sensing since the past three decades, have been briefly discussed. The advent of nanotechnology and its applications in gas sensing and the relevant literature is briefly reviewed. The properties of the gallium nitride nanowires and the metal oxide nanoclusters, used in the study have been presented here.

Chapter 3 gives the step-by-step fabrication details of the nanowire - nanocluster hybrid devices developed. Dielectrophoretic technique, which is widely used for aligning the nanowires for device fabrication is introduced. Microfabrication recipes have been described in detail. Chapter 4 describes the surface morphology, structural and electrical characterization effort for analyzing the nanocluster-nanowire hybrid devices.

Chapter 5 An overview of the gas sensing measurement set-up which has been custom built is given in the first section of the chapter. The sensor measurement results for different nanowire-nanocluster devices have been presented. Responses of the devices to breathing air, nitrogen, alcohols, aromatics, nitro-aromatics, water vapor and interfering agents have been discussed in detail. An attempt is made to explain the sensing behavior based on the current literature and the observed trends.

Chapter 6 makes an attempt to explain the sensing mechanism of the devices fabricated in this work.

Chapter 7 summarizes the important aspects of this research and discusses the possible applications of the sensor technology developed in this work. Finally, emphasis has been laid on the aspects of this work, which require further understanding and which could be of interest for future research.

Chapter 2: -Background

The aim of this chapter is to understand and discuss a few important concepts in the field of semiconducting metal oxides and the effect of dimensionality on their surface properties, which make them highly useful for sensing. A detailed literature search has been performed and reviewed before deciding on pursuing the proposed nanowire-nanocluster (NWNC) sensor technology. Relevant results of the review are presented in this chapter.

2.1 Semiconducting metal-oxides for gas sensing



Figure 2.1: Schematic diagram of the receptor, transducer and the utility functions of a semiconducting metal-oxide layer [17]

The use of semiconducting metal-oxides is one of the most promising techniques, for meeting the demands of the state of the art integrated gas detection systems. They have low production costs and low power consumption along with reasonable sensitivity and stability [18–20]. The metal-oxide sensors detect gases by virtue of their variation in resistance, when they are exposed to gases. The gas sensors offer a wide range of detection capabilities, in view of the market demands for oxygen, inflammable gas and toxic gas sensors. However, the semiconducting metal-oxide sensors suffer from the lack of selectivity.

Sensitivity of these sensors is controlled by three independent factors, receptor function, transducer function and utility as illustrated in the Figure 2.1. The reception function of the sensor material depends on the interaction of gas molecules with the surface. As the metal-oxide layer is exposed to air, the oxygen species are adsorbed on the surface. The surface adsorbed oxygen species deplete the electrons close to the metal-oxide surface creating surface charge depletion. When the sensor is exposed to the target gas (i.e. a reducing gas), the adsorbed oxygen species reacts with it, releasing the electrons back to the metal-oxide semiconductor. The transducer function takes place in the form of conversion of the change in the depletion width to a change in electrical resistance.

Important properties of metal oxides for gas sensing as discussed in [19] are summarized here.

- The sensors with smaller crystalline size show higher sensitivity.
- For the surface of the metal oxide to be able to respond to the analytes by modulation in surface band bending, it is important that the concentration of native surface states be minimized.
- It has been shown that for good sensing action of a gas sensor, the activation energy of chemisorption on the oxide surface should be small and the activation

energy for the desorption of the species should be high.

- Many metal oxides cannot by themselves be used as the chemiresistive sensors. Proper amounts of catalytic noble metal particles can be added to promote the sensing performance.
- Many other factors like the particle crystalline facets, porosity of the metaloxide, intentionally introduced dopants, sensor configuration etc. can influence the performance of gas sensors.

2.2 Why nano?

Nanomaterials and nanostructures are defined as having at least one critical dimension of 100 nanometers or less. At the nanoscale levels, the physical, chemical, and biological properties of materials differ very much from the properties of bulk matter [21]. These properties enable development of highly complex and multifunctional materials and systems, which have tremendous potential in improving our lives in numerous ways.

Nanowires are one-dimensional structures that are cylindrical in shape, with length to diameter ratios often greater than 10^3 . Nanoparticles are zero-dimensional particles sized between 100 nm and 1 nm. Nanowires and nanoparticles are highly functional structures with unique properties arising from their low dimensionalities [22]. As the nanowires are often grown without any substrate, lattice mismatch and thermal expansion coefficient mismatch problems are not present in these structures. This could mean achieving materials that are free from strain, dislocations, and other structural defects. Due to their high surface to volume ratio, the conduction through these nanowires is strongly affected by the chemical species adsorbed on their surfaces [23]. This would enable us to develop extremely efficient chemical and biological sensors. Their large surface to volume ratio also enables effective heat removal in the devices. Photo-generation and light extraction are also enhanced due to large surface area in these structures. As nanowires can be placed on any substrate after the growth is completed, they could be integrated with any platform, including flexible substrates. Once they are placed at pre-determined positions on a substrate, it is relatively simple to apply the conventional fabrication processes to realize electrical and optical devices [14]. This opens up possibilities of integrating III-V compound semiconducting nanowire devices with conventional Si microelectronics. Reduced dimensionality enhances electronic, mechanical, chemical, and optical properties in the nanowires.

2.2.1 Properties of Gallium Nitride nanowires



Figure 2.2: Band structure of wurzite GaN.

Though carbon nanotubes have several advantages, they still suffer from one major drawback - lack of control in selective growth of semiconducting and metallic nanowires [24]. Also, carbon nanotubes do not allow control of their bandgaps, hence opportunities of influencing the chemical reactivity using carbon nanotubes are limited. Semiconducting nanowires, especially compound semiconductors provide greater flexibility as their bandgaps and doping properties can be controlled by alloy and impurity concentrations, respectively.

GaN has an energy gap value that approaches 3.4 eV at room temperature (Figure 2.2) enabling GaN devices to support peak internal electric fields about five times higher than silicon or gallium arsenide (GaAs). Wide bandgap results in lower thermal electron-hole pair generation, hence GaN devices can work at high temperatures. Due to the larger cohesion energies of its constituent atoms, GaN is chemically robust material, less vulnerable to attack in caustic environments, and more resistant to radiation damage [25]. As a result, nanostructures and nanodevices made of GaN and related nitrides can be utilized to achieve nanoscale ultraviolet (UV)/visible light emitters, chemical sensors and radiation hard, high-temperature electronic devices. Integrating these nitride nanodevices with Si microelectronics could eventually lead to single chip solution for complex optical communication elements, bio-detection, chemical sensing systems, etc. Free, air-exposed surfaces of other compound semiconductors (GaAs, InP) exhibit a high density of surface states, which "pin" the surface Fermi-level at a characteristic value. This leads to a high minority carrier surface recombination velocity, which degrades the surface properties. The GaN surface is not pinned, hence, depositing different metal catalysts will have different surface depletion effects, which in turn will enable us to tailor the surface reactivity for different adsorbates.
2.2.2 Properties of metal oxide nanoclusters

Metal oxide nanoparticles have the capability of exhibiting unique physical and chemical properties due to their limited size and high density of corner/edge surface sites. To ensure structural stability, a nanoparticle must have a low surface free energy and as a consequence, the phases that have a low stability in bulk materials can become stable in nanoparticles [26, 27]. Also phenomena like size induced structural distortions and non-stoichiometry are observed in nanoparticles. The nanostructure also produces quantum confinement effects, which arise from the presence of discrete atom-like electronic states [28]. These structural and electronic properties influence the physical and chemical properties of the nanoparticles in general. In the bulk state, many semiconducting metal oxides have wide-band gaps and low reactivity [29]. However, a decrease in the size of the metal oxide nanoparticle changes the band gap, which influences the chemical reactivity [30, 31]. Solid-gas reactions mostly are confined to the surface/interface regions of the solid. As mentioned earlier, in case of nanostructured metal oxides, the unique structural and electronic surface properties result in a surface with unprecedented sorption. Additionally, the presence of under-coordinated atoms or oxygen vacancies in the oxide nanoparticle enhance the chemical activity of the system.

2.3 Review of the state-of-the-art

A lot of work has been done to explore the sensing properties of nanowires formed from materials such as silicon [32, 33], metals [34, 35], metal oxides [36, 37] and polymers [38, 39]. Nanowires are well suited for direct measurement of changes in their electrical properties (e.g. conductance/resistance, impedance) when exposed to various analytes. Prior research has demonstrated the enhanced sensitivity, reactivity and catalytic efficiency of the nanoscale structures. Unfortunately, the surface/adsorbate interactions of the nanowires are limited and non-specific. Despite being electrically sensitive, nanowires still suffer from the same lack of selectivity as their bulk counterpart devices. Debye length L_D for a semiconductor is defined as:

$$L_D = \sqrt{\frac{\varepsilon K_B T}{q^2 n}} \tag{2.1}$$

where ε is the dielectric permittivity, k_B is the Boltzmann constant, T is the absolute temperature, q is the electronic charge, and n is the carrier concentration. For maximum sensitivity, the critical dimension of the nanostructure should be at most twice the Debye length for the material. The GaN nanowires (un-intentionally doped) grown at NIST and by other groups often have carrier concentration in excess of 10^{17} cm⁻³. Thus, at room temperature the Debye length for such a nanowire will be around 10 nm. The growth methods often result in nanowires with average diameter of 100 nm. Thus, it is evident that bare nanowires would only provide limited sensitivity.

The idea of functionalizing or decorating the NW surface with metal or metal oxide nanoparticles or nanoclusters aims at resolving the deficiencies of such bare NW-based sensors. When carefully selected metal/metal oxide nanoparticles are placed on the surface of a nanowire, significant changes can result in the physical properties of the system. Nanoclusters of metals/metal-oxides supported by GaN nanowires will act as nanocatalysts, which will not only increase the sensitivity and



Figure 2.3: (a)Schematic representation of a nanocluster-nanowire hybrid structure assembled on a substrate using post growth assembly method (b) Cross-section of the nanowire showing the spill-over and variations of depletion region due to the adsorbate-nanocluster interaction.

lower the detection time, but also enable us to tailor the selectivity, by incorporating different nanocluster materials. A catalyst has two very important effects when it is placed on a semiconductor surface: (1) spill-over and (2) fermi-level control. Catalysts designed to lower activation energy of a specific reaction often produce ionized active radicals (e.g. H^+ , O^-) from the adsorbed species which can then spill-over to the semiconductor where they can be more effective in charge carrier transfer [40, 41]. Whenever a metal is deposited on a semiconductor, a metal-semiconductor junction is formed. At thermal-equilibrium, the fermi-levels of semiconductor resulting from the charge transfer needed for such a balance. When a metal particle is small enough (high surface-to-volume ratio), adsorption of species on the surface of metal can change the fermi-energy of the metal, which in turn affect the depletion barrier and change the resistance of the semiconductor. The nanoparticles can increase the adsorption of chemical species by introducing additional adsorption sites on the nanowire, thus increasing the sensitivity of such a system. Also, the metal or metal oxide nanoparticles can be selected to act as catalysts designed to lower the activation energy of a specific reaction, which produces active radicals by dissociating the adsorbed species. These radicals can then spill over to the semiconductor, where they can be more effective in charge carrier transfer. Finally, the nanoparticles can modulate the current through the nanowire through the formation of a nanosized depletion region [42], which is in turn is a function of the adsorption on the nanoparticles.

In the last few years, there have been impressive demonstrations of hybrid gas sensors based on nanotube/nanowire decorated with nanoparticles of metal and metal-oxides. Leghrib et al. reported gas sensors based on multiwall carbon nanotubes (CNTs) decorated with tin-oxide (SnO_2) nanoclusters for detection of NO and CO [43]. Using mixed $\text{SnO}_2/\text{TiO}_2$ clusters on CNTs, Duy et al. demonstrated ethanol sensing at a working temperature of 250 C [44]. Balzsi et al. fabricated hybrid composites of hexagonal WO₃ powder with metal decorated CNTs for sensing NO_2 at room temperature [45]. Kuang et al. demonstrated an increase in the sensitivity of SnO_2 nanowire sensors to H_2S , CO, and CH_4 by surface functionalization with ZnO or NiO nanoparticles [46]. ZnO NWs decorated with Pt nanoparticles were used by Zhang et al., and they showed that the response of Pt nanoparticles decorated ZnO NWs to ethanol is three times higher than that of bare ZnO NWs [47]. Chang et al. showed that by the decoration of Au nanoparticles on ZnO NWs, the sensor sensitivity to CO gas could be enhanced significantly [48]. Dobrokhotov et al. constructed chemical sensors from mats of GaN NWs decorated with Au nanoparticles and tested their sensitivity to N_2 and CH_4 [49]. Multiple GaN NWs coated with Pd nanoparticles were employed for the detection of H_2 in N_2 at 300 K by Lim et al. [50].

All these results clearly demonstrate the potential of the nanowire-nanocluster based hybrid sensors. However, there are still fundamental questions and challenges, which have not been investigated properly. Most of the reports are on mats of nanowires. Although this often increases the sensitivity, the complex nature of inter-wire conduction makes interpreting the results difficult. Also, only few reports have actually shown room-temperature operation, and the selectivity is often shown for a very limited number of chemicals. Majority of the highly sensitive hybrid nanowire-nanocluster devices developed so far require high operating temperatures ($T_{oper} > 250 \text{ °C}$) and large response times (more than 5 min). The room temperature operation of nanowire-nanocluster devices was demonstrated by few groups, but reported sensitivities were quite low with long response times. Very few research groups have actually demonstrated the operation of the sensors with air as the carrier gas. The ability of a sensor to detect chemicals in air is what ultimately determines its usability in real-life.

Chapter 3: -Experimental Details

This chapter gives the fabrication details of the sensor devices. The details of nanowire growth using molecular beam epitaxy (MBE) technique are described in brief in the first section. The alignment of the nanowires across the metal electrodes to form single nanowire device, using a technique called dielectrophoresis is described in the following sections. The top contact metallization followed by sputter deposition of nanoclusters and a rapid thermal annealing procedure is also discussed.

3.1 Nanowire Growth



Figure 3.1: Schematic representation of MBE system

The nanowire growth was carried out at NIST (Boulder, CO), in a conventional gas- source MBE system with Knudsen cell Ga, Al, Si, and Be sources and an radio frequency (RF) plasma N source. The schematic of the chamber set up is shown in Fig 3.1. During the GaN nanowire growth, the nitrogen flow was 3 standard cubic centimeter per minute (sccm) and RF plasma power for the N source was 450 W. The growth chamber pressure was approximately 2×10^{-5} Torr, almost all of which was N species from the RF plasma N₂ source. Substrate temperature measurements were made using an optical pyrometer. Silicon (1 1 1) wafers were prepared for growth with a 90 s etch in a 10% HF:H₂O mixture by volume, rinsed for a few seconds in static deionized water, and blown dry with a filtered nitrogen gun. The wafers were outgassed in a preparation chamber at 750 °C for 15 min, then outgassed again at 850 °C for 10 min in the growth chamber. A 0.5 nm layer of pure Al was first deposited at 700 °C, then 50-80 nm of AlN was grown at a temperature of 630 °C. The nanowires were typically grown at a substrate temperature of 820 °C. Schematic and SEM picture of the grown nanowires are shown in Fig 3.2. The growth rates for the nanowires were from 0.1 to 0.2 μ m/h. The typical beam equivalent pressure (BEP) for Ga was 1.0 × 10⁻⁷ Torr.



Figure 3.2: (a) Schematic of the MBE GaN NW growth (b) SEM image of the GaN nanowires grown on Si substrate.

Nucleation of nanowire growth is typically random, producing nanowires of a wide range of densities and diameters within a single growth run. It was found that nanowires nucleated on AlN buffer layers arose from the top of GaN islands with a density that increased with increasing substrate temperature in the range of 740-800 °C while the nanowire growth rate declined. Increasing substrate temperature led to larger diameter nanowire nuclei and thereby reduced the nanowire density. The length of the GaN nanowires varied from 8 um to 15 um whereas the diameters were between 200 nm to 350 nm. More details about the growth and properties of GaN nanowires used in this work have been given in [51] and [52].

3.2 Fabrication of the sensor devices

The key issues in successfully realizing nanowire devices are yield and reproducibility. There is a lot of literature available, on nanowire field effect transistors (FETs), made using e-beam lithography, focused ion beam (FIB) techniques, or atomic force microscopy (AFM) manipulation. In order to develop rapid prototype device structures, a general fabrication technique is needed with desirable characteristics such as:

- Batch fabrication
- Compatibility with standard Si microfabrication technology.
- Suitability for any nanowire material system and for any type of substrate

One needs to develop a fabrication technique that possesses all the above-mentioned characteristics.

3.2.1 Sample Preparation

The starting material was three-inch p -type Si substrates with $(0\ 0\ 1)$ crystal orientation. The wafer is coated with a thick photoresist (Microposit S1813, a positive tone resist) film and is baked for 5 min at 120 °C. This is done in preparation to protect the surface quality of the wafer before the dicing procedure. Wafers were cut using a Microautomation Dicing Saw (Disco 341 Wafer Dicing Saw) into 9 mm \times 9 mm size dies, suitable to fit on to a side-brazed "Dual In-line Package".

After the completion of the dicing process, the samples are cleaned in boiling acetone followed by ultra sound sonication (when the sample is still dipped in acetone) to completely remove the photoresist. The samples are then cleaned in a water based detergent to clean off any unwanted debris and then sonicated in deionized water. The samples are now ready for the standard RCA cleaning, which is a standard set of cleaning steps in semiconductor microfabrication/manufacturing.

- 1. The first step is the removal of insoluble organic contamination. This is performed with a 1:1:5 solution of NH_4OH (ammonium hydroxide) + H_2O_2 (hydrogen peroxide) + H_2O (water) at 80 °C typically for 10 minutes. The samples are then transferred to a DI water bath.
- 2. The second step is a short immersion in a 1:50 solution of HF + H_2O at 25 °C, in order to remove the thin oxide layer (formed during step 1).
- 3. The third step is performed with a 1:1:6 solution of HCl + H₂O₂ + H₂O at 80 °C for another 10 mins. This treatment effectively removes the remaining traces of metal contaminants.

3.2.2 PECVD Passivation layer

After meticulously cleaning the samples, a passivation layer (an 800 nm thick SiO_2 layer in this case) is deposited on them. Plasma enhanced chemical vapor deposition (PECVD) is a technique commonly used in microfabrication to deposit layers of insulating materials and amorphous or polycrystalline silicon. PECVD is relatively cold process with deposition temperature kept at 300 °C and uses energetic electrons from the plasma to dissociate the precursor gases. Though, leakage current in PECVD oxides are known to be higher than high temperature chemical vapor deposition (CVD) processes, this is not a problem in this case as more than 500 nm thick oxide layers are used in this study. The process parameters used for deposition by PECVD are: RF power of 30 W, deposition temperature of 300 °C, gas flows of 400 sccm of Silane (SiH₄) and 900 sccm of Nitrous oxide (N₂O) and a deposition rate of 4.8 nm/s. The thickness of the oxide deposited is monitored by using an Ellipsometer.

3.2.3 Alignment Electrodes

Bottom electrodes are now patterned on samples in order to facilitate the alignment of nanowires using "Dielectrophoresis" (explained in detail in the following section). Alignment electrode geometry determines how efficiently nanowires can be trapped in a pattern. This electrode geometry has also to be compatible with the type of device, which is going to be realized from the nanowires. Two important aspects of the alignment electrode design are a) the height of the electrode, and b) the shape of the electrode. Alignment electrode with large height has higher capture area associated with it but would results in larger stress in the nanowire



Figure 3.3: Different geometries of the alignment electrodes present on the sensor chip.

due to bending. Previous studies indicated that an electrode thickness of 20 nm resulted in a better yield during the alignment procedure[53]. Varied electrode geometries generated different patterns of electric field in between the electrode gap for dielectrophoresis. Fig 3.3 shows the optical microscope images of different electrode designs, which have been investigated in this study. However, in this work no advantage of any particular electrode geometry was observed.

The fabrication process of the alignment electrodes starting with the photolithography step is detailed below:

1. A bi-layer stack of photoresists MicroChem LOR 3A and S1813 was used to

support lift-off process for the metal electrode structures. LOR 3A was spin coated at 4000 rpm for 45 seconds followed by a soft bake at 170 °C for 5 minutes. The S1813 photoresist was then spin coated at 4000 rpm and soft baked at 115 °C for 90 seconds.

- 2. The die coated with photoresist was next exposed to UV illumination through the alignment electrode mask.
- 3. Finally, the exposed sample was developed in Microposit MF 319 developer for 75 s followed by a rinse in DI water. This step opens windows for the metal deposition.
- 4. Ti (20 nm) was deposited on the above prepared sample, using electron-beam metal evaporation (by Denton Infinity 22 E-beam Evaporator) technique.
- 5. Following the metal deposition, the samples were immersed in photoresist PG remover at 75 °C to allow for the metal lift-off.

3.2.4 Dielectrophoretic alignment of the nanowires

As mentioned earlier, there have been some gas sensing studies on mats of nanowires, but interpreting the results become quite complex due to the interwire connections in such a case. Also such devices are not reliable and reproducible. When it comes to individual nanowire manipulation, techniques like electron beam lithography, scanning probe techniques and atomic force microscopy are involved which are often time consuming [54–56]. For an assembling technique to be effective and successful, it should address large-scale simultaneous placement of nanowires with good reliability, reproducibility and compatibility with Si process technology. An electric field assisted alignment technique, which is termed as dielectrophoresis has been used, in this study.

A neutral particle placed in a non-uniform electric field experiences a force due to the interaction of the induced dipole moment with the divergent electric field. This force is called the dielectrophoretic (DEP) force, and the translational motion of the neutral particle caused by this force is termed as dielectrophoresis [57]. Aligning or manipulating particles using the dielectrophoretic force relies on the difference in the polarizability of the particle and the medium used for suspending the particles. Generally the suspending medium is an organic solvent such as isopropanol (IPA), ethanol, acetone etc. Dielectrophoresis is now a widely used technique for directed alignment of nanowires for fabricating nanowire devices because it assists alignment of nanowires across pre-patterned electrodes, which can then be used for establishing electrical contacts with the nanowire ends [58, 59]. A simple model for dielectrophoretic alignment of GaN nanowires has been presented in [60].

Figure 3.4 schematically explains the working principle of the dielectrophoretic alignment of the nanowires. In order for dielectrophoresis to work, the nanowires have to be suspended in a solvent. This is usually done by sonicating the growth matrix in a glass vial (for ~ 10 s) containing suitable solvent (IPA in this case). The energy from the ultrasound breaks the nanowires from the growth matrix and releases them into the solvent. A pre-patterned substrate, in this case titanium electrodes on SiO₂ coated Si substrate, is used for mounting the nanowires to make sensors. When the nanowire suspension is dispersed on a sample using a micropipette, with voltage applied between two metal pads, the divergent electric field interacts



Figure 3.4: Schematic representation of dielectrophoresis set-up.

with the induced electric dipole moment of the nanowire. The DEP force experienced by the nanowire is normal to the sample surface. In case of a positive dielectrophoretic force (determined by the difference in the dielectric permittivities of the nanowire and the dispersing solvent), the nanowires will bridge the pads with complete evaporation of the solvent.



Figure 3.5: SEM images of a single nanowire aligned across the electrodes.

The factors that determine the effectiveness, and subsequently the yield of the alignment process are (a) frequency and amplitude of the applied voltage, (b) diameter and length of the nanowires and (c) the electrode design. An attempt was made to align a single wire across the alignment electrodes to achieve high sensitivity devices. For the fabrication of the devices in this work, alignment voltage was selected in the range of 5 V - 15 V rms and frequency was in the range of 1 kHz-10 kHz, depending on the concentration of the nanowires in the suspension. SEM (scanning electron microscopy) image of one of the fabricated devices is shown in Fig 3.5.

3.2.5 Encapsulation of the nanowires

After completion of the alignment, the sample will be cleaned using oxygen plasma (25 % 0₂ in Argon, 20 mTorr, 50 W, 5 min) to remove the organic residue left after evaporation of the solvent. For ensuring the stability of the aligned nanowires and encapsulating them, a thin 50 nm PECVD oxide is deposited at 300 °C. CVD techniques employ high temperatures (700 - 900 °C) to dissociate the precursor gases, which are unsuitable for maintaining the integrity of GaN nanowires.

3.2.6 Top electrodes

The fabrication of the top electrodes is an important step for establishing ohmic contacts to the nanowire ends. For this purpose, another photolithography step was performed using the bi-layer stack of photoresists LOR 3A and Microposit S1813. A metal stack of Ti (70 nm)/Al (70 nm)/Ti (40 nm)/Au (40 nm) was deposited on the photoresist patterned sample for the formation of the top contacts. A composite layer of aforementioned metals has been shown to form very good ohmic contacts with the n-type GaN nanowires [61].

General metal contact schemes to semiconductors often use multilayer stacks with each layer satisfying a specific purpose. The first layer, which is in contact with the semiconductor, is called the contact layer, and it is often a metal that has good sticking coefficient to the semiconductor surface. The work function of the contact metal has to be matched closely with the electron affinity of the semiconductor to form low resistance contacts. The second metal layer with low resistivity is used to reduce the bulk resistance of the contact. A top metal layer, usually Au for compound semiconductors, which prevents the contacts from oxidation and corrosion, is deposited at the very end. For semiconductor-metal contacts requiring high temperature processing to reduce their contact resistance, a diffusion barrier layer is placed between the top layer (Au) and the bulk layer to minimize diffusion (both in and out diffusions) between the metal layers.

Titanium and aluminum based metallization schemes have been successfully used to form Ohmic contacts to GaN. For n-GaN Ti with a work function of 4.33 eV is the closest match to the electron affinity of GaN, which is about 4.1 eV. Ti provides good adhesion to the GaN surface, producing reliable and reproducible lift-off. GaN surfaces have a very high chemisorption affinity for oxygen. As a result, a native oxide is usually always present on the surface of GaN. This layer acts as an insulating barrier between the metal and the semiconductor. Ti is especially advantageous because it can reduce the GaN native surface oxide upon alloying. Ti has the ability to dissolve small amounts of oxygen and still remain in stable α -Ti phase with oxygen in solid solution with the metal. Solid phase reactions between Ti and GaN forming TiN is possible since the heat of formation of TiN and GaN are 2265 and 2110.9 kJ mol-1, respectively. During annealing N out-diffuses from the GaN lattice to form TiN and nitrogen vacancies are formed in the GaN without decomposing the crystal structure. N vacancies act as shallow donors in GaN. The interfacial region thus becomes heavily doped, reducing the contact resistance.

The present contact scheme uses a reactive barrier layer, which is a Ti layer placed on the top of the standard Ti/Al layer. As a result, during high temperature annealing (750 °C), the Ti and Al layers are expected to undergo enhanced reactions producing $\text{Ti}_x \text{Al}_{1-x}$ intermetallic alloys. Such an alloy produces low resistance contacts. Formation of these intermetallic alloys are extremely beneficial for obtaining a low resistance and extremely reliable ohmic contact to n-GaN.

3.2.7 Sputter deposition of the nanoparticles

The most significant challenge in realizing the nanocluster-nanowire hybrids is controlling the size of the nanoclusters and their coverage over the nanowire surface. Initially various methods including PECVD and dispersion from commercially available colloidal nanoparticle suspensions by spin coatings were considered. After carefully weighing the advantages and disadvantages of each method, the use of e-beam evaporation and RF/DC sputter deposition of the metal/metal-oxide nanoclusters have been adopted for this work. After thorough experimentation, a good nanocluster formation has been observed for the RF/DC sputtering methods when compared to the e-beam evaporation. The availability of a wide variety of binary/tertiary metal oxide sputter targets also justifies this choice. Literature also showed successful nanocluster deposition using the sputter deposition technique [62, 63]. Therefore, for the hybrid metal oxide nanoparticle/GaN nanowire sensors fabricated in this work, the nanoparticles were deposited using the RF sputtering technique (Denton Vacuum Discovery 550). The deposition time was optimized to ensure that the sputter deposited metal oxide formed isolated islands and that the nanoparticles did not coalesce to form a conducting film on the surface.



Figure 3.6: Fabrication steps for the nanocluster-nanowire hybrid sensor devices

The optimized deposition conditions of different nanoclusters on GaN NW's are given below:

• The TiO_2 nanoclusters were deposited on the exposed GaN NWs using TiO_2 target and RF magnetron sputtering. The deposition was done at 325 °C with

50 sccm of Ar flow, and 300 W RF power. The deposition rate was about 0.24 /s.

- For the SnO₂ nanoclusters on GaN NWs, the SnO₂ target was sputtered with an RF power of 200 W in 30 sccm of oxygen and 20 sccm of argon gas flow for 7 minutes, while sample temperature was held at 90 °C.
- For TiO₂-Pt composite NCs, the Pt was sputtered using DC sputtering after annealing of the TiO₂ clusters on GaN NW. The Pt sputtering was done with an Ar flow of 35 sccm, at a pressure of 1.3 Pa and power of 40 W for 10 s.
- For the Pt nanoclusters on GaN NWs, Pt was sputtered on bare GaN NWs after annealing the ohmic contacts at 700 °C for 30 s. The Pt sputtering was done with an Ar flow of 35 sccm, at a pressure of 1.3 Pa and power of 40 W for 10 s.

Fig. 3.6 shows the schematic representation of the overall process steps for the fabrication of the sensor devices made of nanowires coated with metal oxide nanoparticles.

3.2.8 Rapid thermal annealing

A rapid thermal anneal (RTA) is usually employed after the metal contacts are deposited, in order to reduce contact resistance of Ohmic contacts to GaN layers. High performance ohmic contact formation is essential to realize optimum operation of nanowire based devices. The annealing step produces the necessary reactions between the metals and the nitride to form a low resistive contact. In a rapid thermal annealer, the sample is placed inside a thin quartz chamber with halogen lamps surrounding it. As the volume of the chamber is small, the temperature rise rate is extremely high. Even though high rise rates of 25 °C/s are usually used for thin film nitrides, the number of working nanowire devices was quite low when we used this standard rise rate. Rapid rise in temperature during annealing generates stress in the nanowire devices and the nanowires undergo structural breakdown.

RTA was performed for 30 s at 700 °C for the GaN nanowire devices. The temperature ramp rate was 100 °C per minute and the process was performed under a 6000 sccm flow of ultra-high purity Ar. A slower rise rate ensures that the substrate and the nanowire are given enough time to reach equilibrium, hence the stress levels are always kept below the critical limit. In addition to the ohmic contact formation, RTA induces recrystallization of the metal oxide nanoclusters and reduces mechanical stresses in the metal stacks forming the alignment and top electrodes, which is an important consideration for wire bonding the devices.

3.2.9 Device packaging



Figure 3.7: Device packaging (a) One of the wire bonds made to the bond pad (b) Image of the wire bonded device on a chip carrier.

In the final step, bond pads were formed using a thick metal stack of Ti (40 nm)/Au (180 nm) by performing another photolithography step. Formation of bond pads as the last step ensures that the bond pads are not affected by the sputter and the high temperature anneal process. After formation of the bond pads, the devices were mounted on an open top side-brazed 24 pin dual in-line ceramic package and were wire bonded using the wire bonder (Kulicke and Soffa Model 4526).

Chapter 4: -Device Characterization

This chapter describes the surface morphology, structural and electrical characterization effort for analyzing the nanocluster-nanowire hybrid devices. The microstructure and morphology of the sensor devices was characterized by scanning electron microscope (SEM), high resolution analytical transmission electron microscopy (HR-ATEM), Scanning Transmission Electron Microscopy (STEM) and selected area electron diffraction (SAED). The crystallinity and phase analysis was assessed by X-ray diffraction (XRD). electron backscatter diffraction (EBSD) patterns were recorded using an HKL Nordlys II EBSD detector attached to the Hitachi S-4700 SEM. Electrical characterization of the devices was performed by measuring the current-voltage (I-V) characteristics. All the electrical measurements were performed using Agilent B1500A semiconductor parameter analyzer.

4.1 TiO₂ NP/GaN NW devices

The microstructure and morphology of the sputtered material on the GaN nanowires, used for fabrication of sensors was characterized by HR-ATEM and cold fieldemission SEM. The specimens were analyzed in a FEI Titan 80-300 TEM/STEM microscope operating at 300 kV accelerating voltage. The instrument was also equipped with an EDAX Si/Li energy-dispersive X-ray spectrometer and high-angle annular dark-field (HAADF), bright-field (BF), and annular dark-field (ADF) STEM detectors to perform spot, line profile and areal compositional analyses. The instrument was equipped with an X-ray energy dispersive spectrometer (XEDS) and



Figure 4.1: FESEM images of sputter deposited TiO_2 nanoparticles on GaN nanowire surface with deposition times (a) 90 s (b) 214s (c) 343 s.

an electron energy-loss spectrometer (EELS) as well.

4.1.1 Analysis of microstructure and morphology

In order to achieve the optimal size and coverage of the nanoclusters, three samples were prepared with varying sputter time of 90 s, 214 s and 343 s. For these samples, the nanowire suspension solution was dispersed on a SiO₂ coated Si substrate and TiO₂ was sputtered on these randomly dispersed nanowires. These samples were used for SEM microscopy (see Figure 4.1). Rather sparse, well-defined clusters can be seen for both the 214 s and 343 s sputtered coatings of TiO₂. For the 343 s sputtered coating the coverage of the TiO₂ clusters is much denser. The average size of the large clusters, seen in SEM was 15 nm. However, TEM studies revealed the presence of clusters with much smaller diameter (less than 4 nm) on the nanowire surface. For all the sensors only 343 s (corresponding to 8 nm area average thickness) deposits of TiO₂ have been used.

Since the XRD signal from the TiO_2 decorated GaN NWs could not be detected, due to the minuscule volume of TiO_2 nanoclusters, a 150 nm thick TiO_2 film was formed by sputtering it onto a SiO_2 coated Si substrate at 300 °C followed by a



Figure 4.2: XRD Ω - 2 Θ scan of 150 nm thick TiO₂ film deposited on SiO₂/Si substrate at 300 C and annealed at 650 C for 45 s in RTA. All indices correspond to the anatase phase [PDF: 84-1285].

anneal at 650 °C for 45 s in argon. An assumption was made that this processing condition produced an identical morphology as in the case of thinner TiO_2 decoration on the NW. It is identified from the XRD in figure 4.2 that TiO_2 is in the singlephase anatase form. As-deposited TiO_2 films were found to be amorphous (XRD not shown).

The XRD results agree with the TEM analysis on TiO_2 decorated GaN NWs obtained, which revealed that upon annealing at 700 °C for 30 s, the TiO_2 islands became partially crystalline (see figure 4.3). Three most common phases of TiO_2 are anatase, rutile, and brookite. Thermodynamic calculations predict that rutile is the most stable phase at all temperatures and atmospheric pressures [64]. However, comparative experiments with different particle sizes showed that the phase stability



Figure 4.3: Typical morphologies of a 20 nm thick TiO_2 film sputtered on n-GaN nanowires and annealed at 700 °C for 30 s. (a) TEM image showing non-uniformly distributed 2 nm to 10 nm diameter individual TiO₂ particles, some of them are marked by white circles. (b) HRTEM image of an edge of the GaN nanowire with the sputtered TiO2 film, FFT pattern from the red square area in the upper inset indicates 0.35 nm lattice fringes, which are consistent with a (101) reflecting plane of anatase.

might reverse with decreasing particle size, possibly due to surface free energy and surface stress [65]. Anatase is thermodynamically most stable when the particle size is less than 11 nm, whereas rutile is most stable at sizes greater than 35 nm [66]. Although both rutile and anatase TiO_2 are commonly used as photocatalysts, anatase form shows greater photocatalytic activity for most reactions [67, 68]. This is one of the reasons why a TiO_2 film was sputtered for only 343 s (8 nm is the area average thickness in this case) for the sensor fabrication.

Although, 8 nm of TiO_2 was sputtered for fabricating the hybrid sensors, for the



Figure 4.4: (a) BF-STEM image with 5nm to 10 nm TiO_2 nanoparticles barely visible near an edge of a GaN nanowire, some of them are marked by white circles. (b) ADF-STEM image of a TiO₂-containing aggregate on the edge of a GaN nanowire.

TEM studies 20 nm of TiO₂ coating was used. This is done because the thick GaN nanowires prevented acquiring any TEM diffraction with thinner TiO₂ coating. The TEM results presented here for 20 nm thick TiO₂ should be representative of the clusters formed for 8 nm deposited TiO₂ in actual sensors. Typical morphologies of a 20 nm thick TiO₂ film sputtered on n-GaN nanowires and annealed at 700 °C for 30 s are illustrated by TEM data in figure 4.3. The TEM image in figure 4.3(a) shows 2 nm to 10 nm diameter individual TiO₂ particles non-uniformly distributed on the surface of a GaN nanowire. Some of the particles are marked by white circles. Crystallinity of some TiO₂ nanoparticles was observed as shown in the HRTEM image in figure 4.3(b) of nanocrystallites on the edge of a GaN nanowire with the sputtered TiO₂. The fast fourier transform (FFT) pattern from the red square area in the upper inset shows 0.35 nm lattice fringes, which are consistent with a (101) reflecting plane of anatase, but not available in hexagonal wurtzite-type GaN crystals.



Figure 4.5: (a) X-ray spectrum of an individual 5 nm TiO_2 particle shown by the red circle in the image 4.5(a) . (b) EEL spectra recorded on positions 1 (tip of the aggregate) and 2 (edge of the GaN nanowire) as shown in the image 4.5(b), respectively.

Figure 4.4(a) BF-STEM image shows 5 to 10 nm TiO_2 nanoparticles barely visible against the GaN nanowire. An ADF-STEM image of a TiO_2 island on a GaN nanowire is shown in figure 4 (b). The presence of TiO_2 was confirmed by analysis of selected areas as well as of individual particles using XEDS and EELS and nanoprobe capabilities. The X-ray spectrum in figure 4.5(a) of an individual 5 nm TiO₂ particle marked by the red circle in figure 4.4(a) exhibits the TiK α peak at 4.51 keV and the weak OK α peak at 0.523 keV. The NK α peak at 0.39 keV and gallium lines (the GaL series at 1.0 keV to 1.2 keV) and the CK α peak at 0.28 keV are also identified. EEL spectrum (as seen in 4.5(b)) acquired at position 1 marked in figure 4.4(b) (the tip of a TiO₂-containing aggregate) exhibits the TiL edge at 456 eV and the OK edge at 532 eV and also the CK edge at 284 eV. A reference spectrum recorded at position 2 (an edge of the GaN nanowire in the figure 4.4(b)) also reveals traces of titanium and oxygen with the NK edge at 401 eV and the GaL edge at 1115 eV, respectively.

4.1.2 Electrical characterization

I-V characterization was repeatedly performed after i) fabrication of the top electrodes, ii) Sputter deposition of the nanoclusters, iii) rapid thermal anneal of the devices, and iv) device packaging. These measurements assisted in studying the electrical properties of the nanowires and the contacts.

Figure 4.6 shows the I-V characteristics of a GaN NW two-terminal device at different stages of processing. The I-V curves of the as-deposited devices were non-linear and asymmetric. The current decreased when the SiO_2 layer over the NW was etched. However, the current increased with the deposition of TiO_2 nanoclusters. Oxygen adsorption on the bare GaN nanowire surface can introduce surface states [69], resulting in the decrease of the nanowire conductivity. The devices annealed at 700 °C for 30 s showed significant changes in their I-V characteristics with a majority of the devices exhibiting linear I-V curves. This is consistent with the fact that low resistance ohmic contacts to the nitrides require annealing at 700 °C - 800



Figure 4.6: I-V characteristics of a GaN NW two-terminal device in the dark at different stages of processing. The nanowire device measured has a length of 5.35 m and a diameter of 380 nm. The thickness of sputtered TiO₂ film was 8 nm

°C [61].

Figure 4.7 shows the photoconductance of a bare GaN NW device and the TiO_2 coated GaN NW device. The NW devices with TiO_2 nanoclusters showed almost two orders of magnitude increase in the current when exposed to UV light as compared to the similar diameter bare NW devices. Increase of photoconductance due to surface functionalization has been observed in ZnO nanobelts coated with different polymers [70]. This enhancement of photoconductance is often attributed to the separation of photogenerated charge carriers by a surface depletion field, thereby increasing the lifetime of the photogenerated carriers. After the light is turned off, the photo current decays rapidly but not to the dark current value, which is probably



Figure 4.7: (a) Dynamic photocurrent of a bare GaN NW, (b) of a TiO_2 coated (8 nm deposit) GaN NW. The diameters of both nanowires were 200 nm. The applied bias is 5 volt in both cases.

due to the persistent photoconductivity of the NWs [71].

4.2 TiO₂ - Pt composite NP/GaN NW devices

Depositing catalytic metals such as Pt, Pd, and other transition metals onto the surface of oxide photocatalysts (such as TiO_2 and SnO_2) is a well-known method for enhancing their catalytic activity. Pt nanoclusters are deposited on the TiO_2 NP/ GaN NW devices with an aim to enhance the sensitive behavior of the devices. The morphological change as well as the change in the electrical properties of these

composite nanocluster devices are clearly noted in this section.

4.2.1 Morphological and structural characterization of NWNC hybrids

It is challenging to measure the sizes and shapes of small TiO_2 and Pt particles on the surfaces of GaN NWs from greyscale TEM images due to:

- 270 nm to 300 nm thickness of the NWs used in the devices and variations of thickness and curvature across the structure
- diffraction contrast induced particularly by bending of the wires: even similar particles could appear as having different intensities, while local thickness variations of the carbon support film could result in variable contrast affecting the mean intensity values of the particles
- overwhelming domination of electron diffraction in SAED from the GaN NW over the diffraction from TiO₂ and Pt nanoparticles.

To overcome these problems, TEM imaging was conducted under minimal beam intensity conditions close to the Scherzer defocus at highest available accelerating voltage of 300 kV using both stationary beam (bright-field TEM/SAED, phasecontrast high-resolution TEM) and scanning beam (STEM/XEDS) modes. Areas for analyses were selected near the wire's edges and on the amorphous carbon support film in the vicinity of the NWs.

Figure 4.8 shows BF-TEM micrographs of a GaN NW on a thin amorphous carbon support film with TiO_2 coating, before and after the Pt deposition. The SAED patterns showed discrete and continuous ring reflections, which can be assigned to



Figure 4.8: BF-TEM image of a GaN nanowire on a thin amorphous carbon support film with TiO_2 island film coatings sputtered on them: (a) without Pt and (b) after deposition of Pt. Insets show the SAED patterns acquired in thin film areas in the vicinity of GaN nanowires assigned to polycrystalline anatase in (a) and to anatase plus fcc Pt in (b), respectively.

the polycrystalline anatase in figure 4.8(a) and to anatase plus fcc Pt in figure 4.8(b), respectively.

The deposited TiO_2 layer formed an island-like film, where 10 nm to 50 nm partially aggregated particles (see Figure 4.9(a)) were often interconnected into extended two-dimensional networks. This was consistent with SAED and compositional analyses (see 4.11) of deposited TiO_2 films indicating a mixture of polycrystalline anatase and rutile and of the same mixture plus fcc Pt nanoparticles (Figure 4.9(b)), respectively.



Figure 4.9: HRTEM image of a GaN NW with TiO_2 sputtered on them: (a) before Pt and (b) after Pt deposition. White circles in (a) indicate partially aggregated polycrystalline TiO_2 particles on the NW surface and on the supporting carbon film. Blue arrows (image (b), left top enlarged inset) mark Pt clusters decorating a 6 nm diameter particle of titania. The TiO_2 particle exhibits 0.35 nm fringes corresponding to (101) lattice spacing of anatase polymorph. 2 nm to 5 nm thick amorphized surface film indicated by black arrows is also shown.

Pt crystalline particles with 1 to 5 nm size were randomly distributed on the surfaces of TiO₂ islands and sometimes were partially coalesced forming elongated aggregates. In the latter case, significant thickness of the GaN NWs made it difficult to visualize TiO₂ deposits due to the limited contrast difference between TiO₂ and GaN and presence of multiple heavy Pt particles. In spite of these severe limitations, detailed HRTEM and HR-STEM observations revealed 0.35 nm (101) hcp lattice fringes belonging to anatase (see figure 4.9(b), inset) and 0.23 nm to 0.25 nm (111) and 0.20 nm to 0.22 nm (200) fcc lattice fringes belonging to Pt nanocrystallites, respectively, as well as amorphous-like Pt clusters with diameter around 1 nm or less (see figures see 4.10a and b). In the Figure 4.10 HAADF-STEM image shows 1 nm to 5 nm diameter bright Pt nanoparticles and barely visible TiO₂ islands (medium



Figure 4.10: HAADF-STEM of a GaN NW coated with TiO2 and Pt. (a) 1 nm to 5 nm bright Pt nanoparticles (shown by blue arrows) decorating surfaces of a polycrystalline TiO2 island-like film and of a GaN nanowire. Medium grey aggregated TiO2 particles (outlined by dashed white line in a) are barely visible on a thin carbon support in image (a) near the edge of the nanowire. (b) High magnification image of the supporting film near the edge of the nanowire exhibits 0.23 nm to 0.25 nm (111) and 0.20 nm to 0.22 nm (200) fcc lattice fringes belonging to Pt nanocrystallites, blue arrows indicate amorphous-like Pt clusters of 1 nm and less in diameter.

grey) randomly distributed near the edge of the nanowire.

The presence of both TiO₂ and Pt nanocrystallites was confirmed by the analysis of selected areas using XEDS nanoprobe capabilities (see Figure 4.11). The X-ray spectrum in figure exhibits the TiK α peak at 4.51 keV and the weak OK α peak at 0.523 keV. The Pt L-series is also visible between 8.267 keV and 13.268 keV and the Pt M-series at 2.05 keV to 2.217 keV. The NK α peak at 0.39 keV and gallium lines (the GaL series at 1.0 keV to 1.2 keV) and the CK α peak at 0.28 keV were also identified. The intensive MoK α line at 17.478 keV and the MoK line at 19.607 keV belong to the supporting mesh grid material.



Figure 4.11: Areal X-ray spectrum indicating presence of Pt and TiO2.

4.2.2 Current-voltage (I-V) characteristics of the composite NC- NW hybrids

Figure 4.12 shows the I-V characteristics of the GaN/(TiO₂-Pt) and GaN/Pt hybrid sensor devices at different stages of processing. The I-V curves of the asfabricated GaN NW two-terminal devices were non-linear and asymmetric (not clear in figure 4.12(a) due to scale resolution). A small increase in the positive current after the deposition of TiO₂ nanoclusters (curve 2) can be attributed to decreased surface depletion of the GaN NW due to passivation of surface states, and/or the high temperature deposition (325 °C) of the nanoclusters initiating ohmic contact formation. The devices annealed at 700 °C for 30s after the deposition of TiO₂ NCs showed significant change in their I-V characteristics with a majority of the devices



Figure 4.12: I-V characteristics of the hybrid sensor device at different stages of processing: (a) $GaN/(TiO_2-Pt)$ hybrids, and (b) GaN/Pt hybrids.

exhibiting linear I-V curves. Interestingly, Pt NC deposition on TiO_2 coated GaN NWs further increased the conductivity of the nanowire. This is probably due to the fact that the Pt clusters depleted the TiO_2 clusters by removing free electrons; increased depletion in the TiO_2 clusters due to Pt would decrease TiO_2 induced depletion in the GaN NW, leading to an increase in the NW current. With the Pt/GaN hybrids, the current decreases followed by the deposition of Pt (figure 4.12(b)), as expected due to the depletion region formed in the NW under the metal clusters.

It is worthwhile to discuss the nature of the depletion region formed by such nano-sized metal clusters on a semiconductor. It has been shown that the classical Schottky model depletion theory cannot predict accurately the zero-bias depletion width produced by metallic nanoclusters on a semiconductor [72]. According to


Figure 4.13: Depletion depth induced by Pt NCs on GaN and TiO_2 as calculated by equation 4.1.

Zhdanov's model the depletion depth associated with such metal nanoclusters on a semiconductor can be estimated by the relationship [73]:

$$W_d = \sqrt[3]{\frac{3r_c V_{bi}}{2\prod q^2 N_d}}$$
(4.1)

where W_d is the depletion width, r_c is the radius of the nanocluster, V_{bi} is the built-in voltage for the GaN-Pt junction, q is the elementary charge, and N_d is the dopant concentration in the nanowire. Figure shows the calculated zero-bias depletion depth produced in GaN and TiO₂ respectively, as a function of the Pt cluster radius according to equation 4.1. For calculating the depletion depth the effective conduction band density of states in TiO₂ was assumed as 3.0×10^{21} cm⁻³ and point-defect related donor concentration as 1.0×10^{18} cm⁻³ [74, 75]. The electron concentration in the GaN NWs was measured to be $1\,\times\,10^{17}~{\rm cm}^{-3}$ in a separate experiment.

Figure 4.2.2 indicates that even a single Pt NC of 2 nm radius can significantly deplete a 10 nm (average size) TiO₂ cluster. The effect of TiO₂ depletion on GaN NW is hard to compute as it could be influenced by numerous factors including interface states and the particle geometry. Given the very high density of TiO₂ clusters on the NW surface (see figure 4.10(b)), it is clear that the Pt particles mostly reside on the surfaces of TiO₂ NCs. However, from figure 4.2.2, it can be seen that when Pt NCs are directly on GaN, they should deplete the carriers in an even larger region in the GaN NW. This qualitatively explains the relatively larger change in current observed when Pt NC were deposited on bare GaN NWs.

4.3 SnO₂ NP/GaN NW devices

For this class of devices, the two terminal suspended GaN nanowire devices were functionalized with SnO_2 nanoparticles. Structural, morphological and phase analysis of the NP/NW device is carried out in a similar fashion.

4.3.1 Morphological and structural characterization of NWNC hybrids

Deposition time of 7 minutes was optimal for the formation of uncoalesced SnO_2 nanoparticles on the GaN nanowire surface. Fig.4.14 shows the SEM image of sputter deposited SnO_2 nanoparticles on GaN nanowire surface. The I-V measurements were performed to ensure that the substrate was not conducting due to the formation of a thin film of the sputter deposited material on the sample. The conducting



Figure 4.14: SEM image of sputter deposited SnO_2 nanoparticles on GaN nanowire surface with deposition times (a) 7 minutes (b) 15 minutes.



Figure 4.15: XRD Ω -2 Θ scan of a 40 nm thick SnO₂ film after 700°C anneal in argon for 30s. Indices correspond to tetragonal SnO₂ phase (P42/mnm) with a=4.758(3) \mathring{A} and c=3.175(2) \mathring{A} lattice parameters.

channel should only be GaN nanowires even after the sputter deposition of the metal oxide nanoparticles.

As in the case of TiO₂ nanoparticles, the tin oxide nanoparticles were also too small to obtain an XRD signal, therefore a reference sample with the tin oxide film on GaN/sapphire substrate was prepared. SnO₂ was sputtered for 1 hour to form a 40 nm thick film followed by annealing for 30 s at 700 °C with the assumption that the oxide would have crystallinity similar to the device structures that were annealed under the same conditions. XRD results in Fig.4.15 indicate that the SnO₂ film is polycrystalline with the rutile structure. These results were supported by EBSD analysis. Fig. 4.16 shows EBSD from individual SnO₂ clusters on GaN NW, for oxide deposition time of 15 minutes followed by annealing at 700°C for 30 seconds.

Further investigation on the SnO₂ nanoparticles on the GaN NW was performed using HR-ATEM/STEM techniques. For this purpose, SnO₂ was sputter deposited on an array of vertically standing GaN NWs on a silicon substrate, followed by RTA at 700 °C for 30 s to replicate the thermal processing of the device fabrication steps. Finally, the coated NWs were transferred onto a TEM grid. Fig. 4.17 presents a HR-TEM micrograph of a GaN NW fragment decorated with randomly distributed partially coalesced 5 nm to 10 nm tin oxide nanoclusters. As one can see from the figure, the particles exhibit crystallinity. The FFT Fast Fourier Transform pattern from the red square in upper right inset indicates 0.34 nm lattice fringes, which are consistent with a (110) reflecting plane of the tetragonal polymorph of SnO₂.

Simultaneous BF and HAADF (Z-contrast) STEM imaging was employed to enhance visualization of SnO_2 nanoparticles which are often barely visible against the much thicker GaN NWs. Complementary BF- and HAADF STEM images of a tip of a GaN NW coated with SnO_2 are shown in Fig. 4.18(a) and Fig. 4.18(b)



Figure 4.16: FESEM image of the nanowire fragment decorated with tin oxide nanoparticles (a); EBSD patterns of GaN (b) and SnO_2 (c-d) with simulated unit cells in the insets. Unit cells in (c) and (d) indicate random crystallographic orientation of SnO_2 grains on GaN surface. Scale bar in (a) is 100 nm.

respectively. The SnO₂ nanoparticles, dark in (a) and bright in (b) STEM images were found to decorate facets of the nanowire and often form elongated aggregates involving several smaller clusters. Fig. 4.19 presents a spot X-ray spectrum of an individual nanocluster acquired at the nanowire surface (see right inset), revealing the Sn K α_1 line at 25.27 keV, the Sn K β_1 line at 28.48 keV, and the Sn L-series between 3.04 keV and 4.46 keV together with the O K line at 0.52 keV. The Ga K α_1 line at 9.25 keV, the Ga K β_1 line at 10.26 keV, and the Ga L-series between 0.96 keV and 1.30 keV were also observed. However, nitrogen (the N K α line at 0.39 keV) was not detected in this particular case. The C K α_1 line at 0.28 keV, the



Figure 4.17: HRTEM image of a nanowire fragment decorated with randomly distributed 5 nm to 10 nm tin oxide nanoclusters, FFT pattern from the red square in upper right inset indicates 0.34 nm lattice fringes, which are consistent with a (110) reflecting plane of the tetragonal polymorph of SnO_2 .

Cu K α_1 line at 8.05 keV and the Cu K β_1 at 8.90 keV belong to materials of the supporting TEM grid.

4.3.2 I-V characteristics of the SnO₂ NC- NW hybrids

Fig. 4.20 shows the dark current-voltage (I-V) characteristic of one of the annealed SnO_2 NP/GaN NW devices, which has an ohmic behavior.



Figure 4.18: (a) BF-STEM image of a tip of a GaN nanowire coated with 5nm to 10 nm diameter SnO_2 nanoclusters forming densely packed chain-like aggregates. (b) HAADF-STEM image of the same area. SnO_2 clusters, dark in (a) and bright in (b), respectively, decorating the faceted surface of a GaN nanowire.



Figure 4.19: X-ray spectrum of individual SnO_2 cluster acquired in the spot marked by the red cross (inset).



Figure 4.20: Dark I-V characteristic of the annealed ${\rm SnO}_2$ NC- NW device

Chapter 5: -Chemical Sensing

This chapter describes the sensing characterization of the hybrid sensor devices. The first section gives the detail of the gas sensing measurement set-up employed for the sensing measurements. Sensing results for all three types of devices: i) TiO_2 NP/GaN NW sensors ii)(TiO_2 -Pt)composite NP/GaN NW sensors and iii) SnO_2 NP/GaN NW sensors have been discussed in the later sections.

5.1 Gas sensing measurement set-up

For the sensing characterization, each sensor chip was placed in a customdesigned stainless steel test chamber of volume 0.73 cm³ with separate gas inlet and outlet. The test chamber had a quartz window on top for UV excitation. Electrical measurements were performed using Agilent B1500A semiconductor parameter analyzer.

A 25 W deuterium bulb (DH-2000-BAL, Ocean Optics) was used as the light source for UV illumination. The bulb was connected to a fiber optic cable, 600 μ m in diameter, which terminated with a collimating lens placed above the quartz window of the chamber. This set-up provided uniform intensity over the entire sample surface. The wavelength of the light bulb was confined to the range of 215 nm to 400 nm and the recorded intensity was 375 nW/cm² at 365 nm wavelength.

Fig. 5.1 shows the schematic drawing for the gas sensing set up which was used for all the sensing measurements. The bubbler is filled with the liquid analyte to



Figure 5.1: Block diagram of the sensor measurement set-up

be sensed. The first Mass Flow Controller (MFC 1) has a flow rate range between 0.2 sccm - 10 sccm. This is used to adjust the carrier gas flow into the inlet of the bubbler. Analyte vapors were picked up inside the bubbler by the carrier gas and the concentration of the analyte in the carrier gas at the bubbler outlet depends on the vapor pressure of the analyte at the established bubbler temperature. The bubbler temperature for the experimental set-up can be set between -10 °C to 75 °C. The flow of the analyte at the output of the bubbler is given by equation 5.1.

$$F_{analyte,out} = \frac{F_{carrier,in} \times P_{vp}}{(P_{atm} - P_{vp})}$$
(5.1)

where $F_{analyte,out}$ is the flow rate of the analyte vapors at the bubbler output, $F_{carrier,in}$ is the flow rate of the carrier gas at the bubbler input, P_{vp} is the vapor pressure of the analyte in the bubbler at a given temperature and P_{atm} is the atmospheric pressure. However it should be noted that equation 5.1 is valid only for $P_{vp} < P_{atm}$.

A bi-pass value at the outlet of the bubbler was used to turn the flow of the gas mixture on or off into the sensing chamber. The MFC 2, which has a range between 0.2 slpm (Standard Liter Per Minute) to 10 slpm, was used to dilute the analyte concentration using the carrier gas. A pressure controller is installed at the junction to maintain constant pressure in the system. Now, a controlled flow of this mixture (mixture of gases from MFC 1 and MFC 2) was passed into the gas sensing chamber using a third mass flow controller, MFC 3, with range between 2 sccm to 100 sccm.

Compressed, breathing quality air (< 9 ppm water vapor) was used as the carrier gas in all the sensing measurements and the net flow rate (air + analyte vapors) through the chamber was maintained at 40 sccm. All sensing measurements were performed at room temperature under 5 V DC voltage bias.

5.2 Sensing characteristics of the TiO_2 NP/GaN NW devices

5.2.1 Response of the hybrid devices to aromatic compounds

This section gives the sensing test results of TiO₂ nanoparticle/GaN nanowire devices. The current through the bare GaN NW devices did not change when exposed to different volatile organic compounds mixed in air, even for concentrations as high as few percents. On the other hand, the TiO₂ coated hybrid devices responded even to the pulses of 20 sccm airflow. This is not surprising considering the fact that the conduction in most metal-oxides is affected by the presence of oxygen. The response of the TiO₂ nanoparticle- GaN nanowire hybrid sensor to 1000 ppm of toluene in air is illustrated in figure 5.2. Exposure to the VOCs in the dark has no effect on the hybrid device. However, in presence of UV excitation, when 1000 ppm of toluene (mixed in air) was introduced into the gas chamber, the sensor photocurrent decreased dramatically to approximately 2/3 of its base value. After 100 s of gas exposure, the gas flow is turned off and the sensor is allowed to recover at



Figure 5.2: Dynamic response of a single GaN-TiO₂ hybrid device to 1000 ppm of toluene. For each cycle the gas exposure time was 100 s. Inset shows the nanowire device with 8.0 m length and diameter 500 nm. The scale bar is 5 μ m.

room temperature without any additional purging. The repeatability of the sensing action of these hybrid sensors is evident from figure 5.2.

Interestingly, these hybrid sensors did not respond when exposed to methanol, ethanol, isopropanol, chloroform, acetone, and 1, 3-hexadiene, even for concentrations as high as several percents. Also, the photocurrent for these sensors increased with respect to air when exposed to toluene vapors, where as, for every other aromatic compound the photocurrent decreased relative to air as seen in figure 5.3. More than 20 sensor devices were tested and they all exhibited the same trend.



Figure 5.3: Photoresponse of the sensor device to (a) 1000 ppm benzene, toluene, ethylbenzene, chlorobenzene, and xylene in presence of UV excitation (nanowire has a of diameter 500 nm) (b) 200 ppb toluene, benzene, ethylbenzene, and xylene with UV excitation (nanowire has a diameter of 300 nm).

Toluene from different sources have been used and the sensor behavior was the same. Figure 5.3b shows the response of a different device for 200 ppb concentrations of the same chemicals. It is clear that even for toluene concentration as low as 200 ppb the relative change in photocurrent is the reverse of that observed with other chemicals. If the photocurrent in the presence of air for these sensors is used as their baseline calibration, then one can distinctly identify toluene from other aromatic compounds present in air using the fabricated hybrid devices.

The response time is defined as the time taken by the sensor current to reach 90% of the response $(I_f - I_0)$ when exposed to the analyte. The I_f is the steady sensor current level in the presence of the analyte, and I_0 is the current level without the



Figure 5.4: Photoresponse of the sensor device (a) for 100 to 10000 ppm concentration range of toluene (b) for 50 ppb to 1 ppm concentration range of toluene.

analyte, which in this case is in the presence of air. The recovery time is the time required for the sensor current to recover to 30% of the response (I_f - I₀) after the gas flow is turned off [76]. For these sensors, the response and recovery times for ppm levels of benzene, toluene, ethylbenzene, xylene (BTEX) concentrations are 60 s and 75 s, respectively. The response and recovery times for ppb levels of concentrations are 180 s and 150 s, respectively. Most of the nanoparticle decorated nanowire/nanotube sensors reported in the literature working at room-temperatures had response times in minutes [43, 45, 46, 77]. Fast response and recovery times indicate fast adsorption and desorption, which could be attributed to the enhanced reactivity of the nanoscale TiO₂ clusters.

The response of two hybrid devices to different concentrations of toluene in air is shown in figure 5.4. Figure 5.4a shows the change of photocurrent of a 234 nm diameter device when exposed to toluene concentrations from 10,000 ppm down to 100 ppm. Figure 5.4b shows the photocurrent of a sensor device with 170 nm diameter wire for toluene concentrations from 1 ppm to 50 ppb.



Figure 5.5: Sensitivity plots of a GaN-TiO₂ nanowire-nanocluster hybrid device (diameter 300 nm) for benzene, toluene, ethylbenzene, chlorobenzene, and xylene. The plot identifies the sensor's ability to measure wide range of concentration of the indicated chemicals.

Sensitivity has been defined as,

$$Sensitivity = \frac{R_{gas} - R_{air}}{R_{air}}$$
(5.2)

where R_{gas} , R_{air} are the resistances of the sensor in presence of the chemical-air mixture and in presence of air, respectively.

The sensitivity plots of a hybrid device for different VOCs tested are shown in Figure 5.5. The sensitivity plot emphasizes the ability of these hybrid sensors to reliably detect BTEX (benzene, toluene, ethylbenzene, and xylene) - the common indoor and outdoor pollutants with wide detection range (50 ppb to 1%).

5.2.2 Response of the hybrid devices to nitro-aromatic compounds



Figure 5.6: Photoresponse of the sensor device to (a) 100 ppb of benzene, toluene, nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene and trinitrotoluene in the presence of UV excitation (b) different concentrations of trinitrotoluene.

The response of the TiO_2 coated hybrid devices when exposed to a concentration of 100 ppb of the aromatics and nitro-aromatics in air can be seen in figure 5.6a. Also, as mentioned earlier, the photocurrent for these sensors increased with respect



Figure 5.7: Sensitivity plot of a GaN-TiO₂ nanowire-nanocluster hybrid device for benzene, toluene, nitrotoluene, nitrobenzene, DNT, DNB and TNT.

to air when exposed to toluene vapors, whereas for every other aromatic compound the photocurrent decreased relative to air. The response is observed to increase with the increase in the number of nitro groups attached to the aromatic compound (see fig. 5.6a).

The response of the hybrid device to different concentrations of TNT in air from 8 ppm down to as low as 500 ppt is shown in figure 5.6b. The response and recovery times of the sensor devices are measured as explained in the previous subsection. The response and recovery times of the nano-devices to different concentrations of



Figure 5.8: Sensitivity of two different GaN nanowire- TiO_2 nanocluster hybrid sensors to 100 ppb of the different aromatic compounds.

TNT are ~ 30 s. The response and recovery times of the rest of the compounds varied from 60 s to 75 s.

The sensitivity is calculated as in equation 5.2. The sensitivity plot of a hybrid device for the different aromatics and nitro-aromatics tested is shown in Figure 5.7. The sensitivity for 1 ppm of TNT is 10%. The devices exhibit a very highly sensitive and selective response to TNT when compared to interfering compounds like toluene. Toluene shows an increase in response with respect to air whereas; TNT shows a remarkable decrease when compared to air. The plot identifies the sensor's ability to measure wide range of concentrations of the indicated chemicals. The sensitivity of two different devices to the different aromatic compounds can be

Table 5.1: I	Performance	$e ext{ of GaN/TiO}_2$	NWNC ł	iybrid se	ensors to	TNT	in co	omparison
with recent	literature.	All the sensors	s operate	at room	tempera	ature		

	Response/ recovery times	Lower de- tection limit	Carrier gas	References
GaN/TiO ₂ NWNC hybrid sensor	30 s/45 s	500 ppt	Air	[78]
Single walled CNTs	$\sim 5 \text{ min}/\sim 3 \text{ min}$	8 ppb	Air	[79]
ZnO nanowires	$\sim 5 \text{ min}/\sim 3 \text{ min}$	60 ppb	Air	[79]
3-aminopropyl triethoxy silane func- tionalized Si NW's	$\sim 8 \text{ min}/\sim 3$ min and recovered only by washing with a solution	$1 \times 10^{-6} \text{ ppt}$	Liquid	[80]

seen in Figure 5.8. Table 5.1 compares the performance of the sensor with the most recent literature for sensing traces of TNT vapors.

5.3 Sensing characteristics of the TiO_2 - Pt composite NP's/GaN NW devices

The most remarkable and significant result of this study is the fact that after the deposition of Pt nanoclusters on the GaN/TiO_2 hybrids, the sensors were no longer sensitive to benzene and other aromatic compounds, but started responding only to hydrogen, methanol, and ethanol. In addition, the $GaN/(TiO_2-Pt)$ hybrids showed no response when exposed to higher carbon-containing (C>2) alcohols such as n-propanol, iso-propanol, and n-butanol.



Figure 5.9: (a) UV photo-response of the GaN/(TiO₂-Pt) hybrid device to 1000 mol/mol (ppm) of methanol, ethanol, and water in air, and hydrogen in nitrogen. The air-gas mixture was turned on at 0 s and turned off at 100 s. (b) Cyclic response of the GaN/(TiO₂-Pt) hybrid device when exposed to 2500 mol/mol (ppm) of hydrogen in nitrogen. The bias voltage for all the devices was 5 V.

Figure 5.9 shows the change of photocurrent of a GaN/(TiO₂-Pt) sensor in presence of 20 sccm flow of air mixed with 1000 ppm of methanol, ethanol, and water, together with 1000 ppm hydrogen mixed in nitrogen. The change in photocurrent for the sensor when 20 sccm of breathing air is flown through the test chamber serves as a reference for calculating the sensitivity of the sensors (the sensitivity has been defined in equation 5.2). R_{air} in eq 5.2 is replaced with $R_{nitrogen}$ for sensing hydrogen.

It is worth mentioning that the GaN/TiO_2 hybrids without Pt showed no response to hydrogen, and the alcohols. Interestingly, when same nominal thickness of Pt NC-coated GaN NW hybrids (GaN/Pt) were tested, they showed very limited



Figure 5.10: Comparative sensing behavior of the three hybrids for 1000 mol/mol (ppm) of analyte in air: gray bar graphs represent GaN/TiO_2 hybrids, gray and maroon represent $GaN/(TiO_2-Pt)$ hybrids, and maroon plot represents GaN/Pt hybrids. Other chemicals which did not produce any response in any one of the hybrids are not included in the plot. The zero line is the baseline response to 20 sccm of air and N₂. For this plot the magnitude of the sensitivity is used. The error bars represent the standard deviation of the mean sensitivity values for every chemical computed for 5 devices with diameters in the range of 200 nm - 300 nm.

sensitivity only to hydrogen and not to any alcohols. The comparative summary of the sensing behavior of the three different hybrids are presented in figure 5.10.

The response of the GaN/(TiO₂-Pt) NWNC sensors to different concentrations of methanol in air is shown in figure 5.11a. Figure 5.11b shows the response to different concentrations of hydrogen in nitrogen for the same sensor device. The sensor response is much higher for hydrogen compared to methanol and ethanol. The response time is also much shorter for hydrogen as compared to methanol, and



Figure 5.11: (a) Photo-response of $GaN/(TiO_2-Pt)$ hybrid device to different concentrations of methanol in air. (b) Photo-response of the same device to different concentrations of hydrogen in nitrogen. The air-gas mixture was turned on at 0 s and turned off at 100 s.

the sensor photocurrent saturates after initial 20 s exposure.

The response time for hydrogen is ~ 60 s, whereas the response time for ethanol and methanol is ~ 80 s. The sensor recovery time for hydrogen is ~ 45 s and the recovery times for ethanol, methanol are ~ 60 s and ~ 80 s, respectively. For comparison, Wang et al. [81] demonstrated ZnO NW-based hydrogen sensor with a response time of 10 minutes for 4.2 % sensitivity. The ZnO NW-based hydrogen sensor reported by Lupan et al. [82] showed a sensitivity of 34 % for a response time of 64 s.

The sensitivity plot of a $GaN/(TiO_2-Pt)$ hybrid device for the various analytes tested is shown in figure 5.12(a). It is to be noted that the lowest concentration detected for methanol and hydrogen (1 ppm) is not the sensor's detection limit, but



Figure 5.12: (a) Sensitivity plot of the $GaN/(TiO_2-Pt)$ hybrid device to ethanol, methanol, and water in air and to hydrogen in nitrogen ambient. (b) Comparison of the sensitivity of $GaN/(TiO_2-Pt)$ and GaN/Pt devices to different concentrations of hydrogen in nitrogen.

a system limitation. It can be seen that the sensor is more sensitive to methanol than ethanol for concentrations ≥ 1000 ppm, and the relative sensitivity switches for concentrations of 500 ppm and below. Similar behavior is observed with twenty devices. Figure 5.12(b) is a comparative plot showing the sensitivity of GaN/(TiO₂-Pt) and GaN/Pt hybrid sensors to hydrogen in nitrogen. The GaN/Pt hybrid devices showed relatively low sensitivity with detection limit of 50 ppm, below which the devices stopped responding. The gas exposure time was also increased to 200 s for the GaN/Pt devices to obtain increased response compared to 100 s for the GaN/(TiO₂-Pt) GaN devices. The sensitivity of the GaN/(TiO₂-Pt) sensors is greater for alcohols and hydrogen when compared with the same concentrations of water in air, which should enable their use in high-humidity conditions.

Table 5.3 and Table 5.2 compare the performance of $GaN/(TiO_2-Pt)$ NWNC sensor devices with the most recent literature in terms of operation temperature, carrier gas, lower detection limit, and response/ recovery times. Though the literature study is not exhaustive, the comparison is intended to show that the fabricated sensor devices have good response to very low concentrations of analytes at room temperature, with air as the carrier gas.

5.4 Response of the SnO_2 NP/GaN NW devices

The response of SnO_2 NP/GaN NW devices to air, nitrogen, alcohols, water, acetone and possible interfering gases has been shown in this section. All the sensing measurements were performed in the presence of UV light. Negligible response was observed towards all the gases in the absence of UV illumination. Similar to the response of TiO₂ NP/GaN NW devices, these devices show a decrease in current when exposed to air flow and an increase in current when exposed to nitrogen gas

Table 5.2: Performance of GaN/(TiO_2-Pt) NWNC hybrid sensors to hydrogen in comparison with recent literature

	Response/ recovery times	Lower detec- tion limit	Temperature	References
$GaN/(TiO_2-Pt)$ NWNC hybrid sensors	60 s/ 45 s	1 ppm with sensitivity of 4%	RT	[83]
CNT films	5-10 min	10 ppm	RT	[84]
SWCNT/ SnO_2	2-3 s	300 ppm	250 °C	[85]
Pd/CNTs	300 s	30 ppm with sensitivity of 3%	RT	[86]
Pd/ Si NWs	1 hr	3 ppm	RT	[87]
$\begin{array}{c} Pd \ doped \ SnO_2 \\ NWs \end{array}$	few min	100 ppm	100 °C	[88]

	Response/ recovery times	Lower de- tection limit	Carrier gas	Temperature	References
GaN/(TiO ₂ - Pt) NWNC hybrid sen- sors	80 s/75 s	100 ppb with 1% sensitivity	Air	RT	[83]
CNT/SnO2 core shell nanostruc- tures	1 s/10 s	10 ppm	Air	300 °C	[89]
MWCNTs/ NaClO ₄ / polypyrrole	20 s/20 s	18,000 ppm	Air	RT	[90]
Metal- CNT hybrids	2 min	500 ppb with sensitivity < 1%	N_2 in a vac- uum test chamber	RT	[91]
V_2O_5 nanobelts	50 s/50 s	5 ppm	Air	150-400 °C	[92]
ZnO nanorods	3.95 min/ 5.3 min	10 ppm	Synthetic air	125-300 °C	[93]
ZnO nanowires	10 s/55 s	1 ppm	Air	220 °C	[94]
ITO nanowires	2 s / 2 s	10 ppm	Air	400 °C	[95]
$Sn\overline{O_2}$ nanowires	2 s / 2 s	10 ppm	Air	300 °C	[96]

Table 5.3: Performance of $GaN/(TiO_2-Pt)$ NWNC hybrid sensors to ethanol in comparison with recent literature

flow.



5.4.1 Response to alcohols

Figure 5.13: Response of the SnO_2 device to (a) different concentrations of methanol (b) 500 ppm of different alcohols.

The SnO_2 NP/GaN NW devices were tested for a response to methanol, ethanol, n-propanol, isopropanol, n-butanol, and isobutanol. An increase in current was observed when the devices were exposed to the alcohol vapors. The response of the device to different concentrations of methanol vapor has been shown in Fig. 5.13(a). As expected, the response of the device increases with an increasing concentration of methanol. Relative response of the device to different alcohols has been shown in 5.13(b) and Fig. 5.14. The devices had maximum response for methanol. A clear trend of a decrease in the response with an increase in the length of the carbon chain in the alcohol molecule was observed. Response towards the straight chain isomer of an alcohol was greater than the response towards the branched isomer of the same alcohol.



5.4.2 Response to acetone, benzene and hexane

Figure 5.14: Response of the SnO_2 NP/ GaN NW device to various chemicals

Fig. 5.14 also shows the response of SnO_2 device to 500 μ mol/mol (ppm) of some of acetone, and hexane vapors. As seen from the figure, the response for acetone and hexane was comparable to the response for isobutanol, the alcohol producing the least response from the device. Negligible response was observed for benzene vapors.

Table 5.4 gives a comparison of some of the current state of the art nanowire alcohol sensors. The alcohol sensors demonstrated in this work can detect alcohol vapors up to 200 ppb which is less than any of the room-temperature operating alcohol sensors as per the data that could be gathered. Most sensors operational at

	Selectivity	Detection limit	Tempera- ture	Response and recov- ery time	References
SnO ₂ /GaN NWNC hybrid sensors	methanol, ethanol, propanol, butanol	100 ppb	room temper- ature	$\begin{array}{ll} {\rm response} & \approx \\ 120 & {\rm s}; & {\rm re-} \\ {\rm covery} & \approx & 80 \\ {\rm s} \end{array}$	[97]
WO ₃ nanoplates	methanol, ethanol, propanol, butanol	1 ppm	260°C-360°C	< 15 s	[98]
ZnO nanowires	ethanol	5 ppm	$170^{\circ}C-230^{\circ}C$	not available	[99]
$\begin{array}{c c} Branched SnO_2\\ nanowires\\ on metallic\\ nanowire back-\\ bone \end{array}$	ethanol	500 ppb	300°C	response 2 s-4 s; recovery \approx 50 s	[100]
$ZnSnO_3$ nanowires	ethanol	1 ppm	300°C	$\approx 1 \text{ s}$	[101]
V_2O_5 nanobelts	ethanol	5 ppm	200°C	$\approx 30 \text{ s-}50 \text{ s}$	[92]
$\begin{array}{c c} p-type & Sb-\\ doped & SnO_2\\ nanowires [102] \end{array}$	ethanol	40 ppm	room temper- ature	$\begin{array}{l} {\rm response} \sim 10 \\ {\rm s; \ recovery \ 40} \\ {\rm s-90 \ s} \end{array}$	[102]
Mixture of tin dioxide and zinc oxide pow- ders in various proportions	ethanol	1 ppb	350°C	Data unavail- able	[103]

Table 5.4: Comparison of the current state of the art nanowire alcohol sensors.

room temperature demonstrated response only up to ppm level of concentration.

5.5 Summary

The summary of the response of all three kind of sensor devices towards different chemicals is listed in the table 5.5.

Table 5.5 :	Summary	of the	response	of NWNC	devices t	to different	analytes.

Type of Device	Analytes
TiO ₂ NP/GaN NW devices	Benzene, Toluene, Ethyl Benzene, Chlorobenzene, Xylene, TNT, DNT, NT, DNB, NB
(TiO ₂ - Pt) NP/GaN NW de- vices	Ethanol, Methanol, Hydrogen
$SnO_2 NP/GaN NW$ devices	Methanol, Ethanol, Propanol, Butanol

Salient features of the sensor devices are enumerated below.

- 1. Selectivity can be tailored for any gas with the design of the different nanoclusters.
- 2. Wide dynamic range (ppb to % sensitivity), with ability to reconfigure the range in real-time.
- 3. Room-temperature and low power operation.
- 4. Fast response and recovery times.
- 5. Standard semiconductor fabrication techniques are used, so they can be manufactured in large scale with low cost and multi-analyte function in one chip.

Chapter 6: -Sensing Mechanism

This chapter makes an attempt to explain the sensing mechanism of the devices fabricated in this work.

6.1 Sensing mechanism of hybrid TiO₂ NP/GaN NW sensors

Figure 6.1 demonstrates a possible mechanism which can qualitatively explain the hybrid sensor's response to different analytes. Although there are still debates over the exact mechanisms for the photocatalytic processes on the TiO₂ surface, it is now well-established that the oxygen vacancy defects (Ti³⁺ sites) on the surface of TiO₂ are the "active sites" responsible for adsorption of species like oxygen, water, and organic molecules [104]. It is interesting to note that a relatively defect free TiO₂ surface, generated by annealing in high-oxygen flux, is chemically inactive [105].

It has been revealed in both experimental studies and simulations that molecular oxygen is chemisorbed on the surface vacancies (Ti^{3+} sites) acquiring a negative charge as shown in figure 6.1(a) [106, 107]. This is believed to be due to the presence of the localized electron density at or near exposed Ti^{3+} atoms on the TiO_2 surface [108]. Water could also be present on the TiO_2 cluster surface via molecular or dissociative adsorption (producing OH^- species) on the defect sites [109, 110]. Although most of the theoretical and experimental studies on oxygen and water adsorption are done for the (110) surface of rutile phase, there are some studies



Figure 6.1: Schematic representation of the GaN (Nanowire)-TiO₂(Nanocluster) hybrid sensor (a) in the dark showing surface depletion of the GaN nanowire, (b) under UV excitation, where photodesorption of O_2 due to hole capture is shown.

that suggest that similar adsorption behavior is also expected for the anatase surface [111]. The GaN NW has the surface depletion region as shown in the figure 6.1(a) which determines its dark conductivity [71]. In the presence of UV excitation above the bandgap energy of anatase TiO_2 (3.2 eV) and GaN (3.4 eV), electronhole pairs are generated both in the GaN NW and in the TiO_2 cluster as shown in figure 6.1(b). Photogenerated holes in the nanowire tend to diffuse towards the surface due to the surface band bending. As mentioned before, this effect of separation of photogenerated charge carriers results in longer lifetime of photogenerated electrons, which in turn enhances the photoresponse of the nanowire devices in general. On the TiO_2 cluster surface however the photogenerated charge carriers lead to an interesting phenomenon - photodesorption of molecular oxygen via capture of photogenerated holes [112]. Oxygen species are often thought to be as efficient electron scavengers. However in n-type semiconductor oxides such as ${\rm TiO}_2$ the surface adsorption produces upward band-bending which drives the photogenerated holes towards the surface. The chemisorbed oxygen molecule (O^{2-}) can readily donate an electron to the approaching hole and desorb as gas as shown in figure 6.1(b) [113]. This process is dynamic in nature, i.e., the desorbed molecules can readsorb on the surface. The increase of photocurrent through these hybrid sensors when exposed to 20 sscm of air is due to the increase in oxygen concentration at the surface of TiO_2 clusters leading to an increase in trapping of photogenerated holes at the surface. This process results in the increase of lifetime of photogenerated electrons. As these nanowires are n-type, excess negative charge on the surface of the wire (on the TiO_2 clusters) will reduce the nanowire current, which can be thought of as the local-gating effect due to charge accumulation on the TiO_2 clusters. There could be other effects such as diffusion of carriers between the clusters and the nanowire,



Figure 6.2: Photoresponse of the sensor device to (a) 1000 ppm of Benzene and Toluene mixed in air and nitrogen (b) different concentrations of water in air.

which could have a major role in the sensing properties of these hybrids.

6.1.1 Response to air, nitrogen and water

The hypothesis could also explain the sensor response when exposed to N_2 flow, as shown in figure 6.2a. In the presence of 20 sccm of N_2 flow, the photocurrent in these sensors increased significantly in comparison with 20 sccm of air flow. In N_2 environment, the oxygen is desorbed from the surface vacancy sites by capturing photogenerated holes, but does not get readsorbed, hence, results in a significant reduction of hole capture. So, the photogenerated electron-hole pairs recombine effectively in the cluster. Thus, the photocurrent through the nanowire/nanocluster hybrid is increased as the local-gating effect due to the TiO₂ clusters is absent in the N_2 environment. In the presence of water in air the photocurrent through these sensors recover towards the level with the air flow as seen in figure 6.2b, indicating a possible reduction of the hole trapping due to adsorption of water on the TiO_2 surface. Water could be adsorbed as a molecule on the defect sites replacing O_2 [114]. With increasing water concentration more defects are being filled with water. However, if the adsorbed water dissociates, producing OH^- radicals, then it is a possibility that they can also act as hole traps and decrease the photocurrent the same way as the photodesorption of oxygen does. Perhaps there is a competition between the molecular water adsorption (reducing hole capture) and dissociative water adsorption (increasing hole capture), with the dominant process ultimately determining the photocurrent level in the nanowires in the presence of water.

6.1.2 Response to aromatic compounds

Presence of aromatic compounds in air such as benzene, ethylbenzene, chlorobenzene, and xylene reduced the photocurrent as seen in figure 6.2a. Organic molecules are known hole-trapping adsorbates [115], although details of the trapping mechanism remain elusive. Most aromatic compounds show high affinity for electrophilic aromatic substitution. There is a much debate about the exact mechanism of photooxidation of adsorbed organic compounds on TiO_2 . However, there exists a significant body of literature that indicate that oxidation may occur by either indirect oxidation via the surface-bound hydroxyl radical (i.e., a trapped hole at the TiO_2 surface) or directly via the valence-band hole before it is trapped either within the particle or at the particle surface [116, 117]. It can be speculated that in the presence of air (with residual water) hydroxyl mediated hole transfer to adsorbates such as benzene, xylene is dominant, where as in N₂ environment direct transfer of valence band holes to aromatic adsorbates could be possible. Despite the mechanism, presence of additional hole traps will reduce the sensor photocurrent as observed in the presence of benzene mixed with N_2 and air (see figure 6.2a). This model can at least qualitatively explain the observed trends observed for four compounds tested namely benzene, ethylbenzene, chlorobenzene, and xylene. Toluene, however exhibits a different trend, which cannot be explained by hole trapping mechanism. There could be other second order effects that are difficult to speculate without fundamental surface studies.

The above interpretation is further validated as the ionization energies of various compounds tested is compared with the responses they generated when the sensor devices are exposed to them(see Table 6.1). The effectiveness of the process of hole transfer to the adsorbed organic molecules should be related to its ability to donate an electron (i.e. the lower the ionization energy of a compound, the easier for it to donate an electron or capture a hole). The observed sensitivity trend for benzene (lowest sensitivity), ethylbenzene, and xylene (highest sensitivity) can be correlated to their ionization energies as show in table 6.1, with benzene being the highest and xylene the lowest among the three.

It is clear from table 6.1 that this trend holds true only for aromatics as 1,3hexadiene did not produce any response in the sensor devices. Although most functional groups with either a non-bonded lone pair or p-conjugation show oxidative reactivity towards TiO_2 [118], aromatic compounds are more easily photocatalyzed than aliphatic ones under the same conditions [119].

6.1.3 Response to nitro-aromatic explosive compounds

As mentioned in the earlier subsection, the effect of separation of photogenerated charge carriers under UV excitation results in a longer lifetime of photogenerated
Organic Compound	Sensitivity	Ionization Potential (eV)
Chloroform	No	11.37
Ethanol	No	10.62
Isopropanol	No	10.16
Cyclohexane	Yes	9.98
Acetone	No	9.69
Benzene	Yes (Min)	9.25
Chlorobenzene	Yes	9.07
Toluene	Yes	8.82
Ethyl benzene	Yes	8.77
Xylene	Yes (Max)	8.52
1,3-Hexadiene	No	8.5

Table 6.1: Physical Properties of various compounds tested

electrons, which in turn enhances the photoresponse of the nanowire devices in general. Since the nitro-aromatic compounds are highly electronegative, they tend to attract electrons from other molecules through charge transfer. This charge transfer between the adsorbed specie on the TiO_2 nanocluster and the nitro groups in the nitro-aromatic compounds increases the width of the depletion region in the nanowire device, reducing the current. A clear trend is observed with the increase in the number of nitro groups attached to the benzene-ring.

6.2 Sensing properties of (TiO₂-Pt) multicomponent nanocluster- GaN nanowire devices

After the deposition of Pt nanoclusters on the GaN/TiO_2 hybrids, the sensors were no longer sensitive to benzene and other aromatic compounds, but responded only to hydrogen, methanol, and ethanol. In addition, the $GaN/(TiO_2-Pt)$ hybrids showed no response when exposed to higher carbon-containing (C>2) alcohols such as n-propanol, iso-propanol, and n-butanol. Understanding the exact selective sensing mechanism is complicated. However, a qualitative understanding can be developed considering how different molecules adsorb on the nanocluster surfaces, and determining the roles of intermediate reactions in determining the sensitivity of the NWNC sensors.

6.2.1 Response of the $GaN/(TiO_2-Pt)$ hybrid sensors to air, nitrogen, and water

It is well-established that the oxygen vacancy defects (Ti^{3+} sites) on the surface of TiO_2 are the "active sites" for the adsorption of species like oxygen, water, and organic molecules [104, 110]. It has been observed that oxygen adsorption on photocatalyst powders such as TiO_2 and ZnO quenches the PL intensity, while adsorption of water produces an enhancement of the PL. Mayer et al. [120] and Anpo et al. [106] proposed that electron-trapping adsorbates, such as oxygen, increase the band-bending of TiO_2 , which facilitates the separation of photogenerated electron-hole pairs in the oxide. Subsequently the PL intensity is decreased as the photogenerated charge carries cannot recombine efficiently. Conversely, in the case of water, the band bending is reduced, resulting in an increase in the PL intensity. In explaining the observed behavior of the hybrid sensors, one has to also consider the depletion effect induced by the TiO_2 clusters on the GaN NW, which is complicated. Considering an inverse relationship, i.e., increase in depletion of the TiO_2 cluster leads to a decrease in the depletion width in the GaN NW and vice versa, some of the observed sensing behavior can be explained.

As depicted in figure 6.3, when oxygen is adsorbed on the TiO_2 NC surface, the



 E_c is conduction band-edge with photogenerated electrons E_v is valance band-edge with photogenerated holes \bigcirc are photogenerated charge carriers

Figure 6.3: Schematic representation of the depletion in the TiO_2 NC in presence of oxygen and water, and its effect on the photogenerated charge carrier separation in GaN NW. Circles in valence band indicate holes and circles in conduction band indicate electrons. depletion width in the NC increases, leading to a decrease in the depletion width in the NW. Adsorption of water, nitrogen, and alcohol produce the reverse effect: they decrease the depletion width of the TiO_2 NC, leading to an increase in the band-bending on the GaN NW surface. Increased band-bending in the GaN NW would result in an effective separation of charge carriers, leading to an increase in photocurrent through the NW. This qualitatively explains the increase in the photocurrent when the hybrid sensor is exposed to water mixed with air or with pure nitrogen (figure 6.4). However, it fails to explain the increase in the photocurrent when exposed to 20 sccm of air flow. Under air flow, more oxygen should adsorb on the NCs, causing an increase in the depletion width of the cluster. This should have resulted in a decrease in the photocurrent based on the assumption made, however, an increase in the photocurrent (figure 6.4) is observed when 20 sccm of air is passed through the chamber. The reason for this behavior is not clear at this time.

In the absence of UV light, the absorption or desorption of chemicals from the cluster surfaces cannot modulate the dark current through the nanowire. In dark, the surface depletion layer of the GaN NW is thicker compared to under UV excitation [121], and also the minority carrier (hole) concentration is significantly lower. Thus the NCs are ineffective in modulating the dark current through the NW.

6.2.2 Response to alcohols and hydrogen

Adsorption of alcohols (RCH₂-OH) on TiO_2 surface can lead to their oxidation [122]. Although there are various mechanisms of oxidation of adsorbed alcohols on TiO_2 surface, the oxidation of alcohols by photogenerated holes has been focused in



Figure 6.4: Photo-response of the $GaN/(TiO_2-Pt)$ device to 1000 mol/mol of ethanol in air and nitrogen, and to 1000 mol/mol of water in air. The devices did not respond to water in nitrogen. The air-gas mixture was turned on at 0 s and turned off at 100 s.

this study. The process can be described by the following reactions [122]:

$$\operatorname{RCH}_2\operatorname{-OH}(g) \to \operatorname{RCH}_2\operatorname{-OH}(\operatorname{ads.})$$
 (6.1)

$$\operatorname{RCH}_2\operatorname{-OH}(\operatorname{ads.}) + \operatorname{h}^+ (\text{photogenerated hole}) \to \operatorname{RCH}_2\operatorname{-OH}^+(\operatorname{ads.})$$
(6.2)

$$\operatorname{RCH}_2\operatorname{-OH}^+(\operatorname{ads.}) \to \operatorname{RCH-OH}(\operatorname{ads}) + \operatorname{H}^+(\operatorname{ads.})$$
 (6.3)

$$\text{RCH-OH(ads.)} \to \text{RCHO(ads.)} + \text{H}^+(\text{ads.}) + \text{e}^-$$
(6.4)

where (ads.) and (g) represent adsorbed and gas phase species, respectively. For equation 6.4 to proceed in the forward direction, the H⁺ species should be removed effectively. It is possible that from TiO_2 NCs the H⁺ species can spill-over on to Pt clusters nearby, where they can be reduced to form H_2 :

$$2 \text{ H}^+(\text{ads}) + 2 \text{ e}^- \rightarrow \text{H}_2 \text{ (g)}$$
 (6.5)

As H^+ reduction and hydrogen-hydrogen recombination is weak on the bare TiO_2 surface [123], the rate of alcohol oxidation to aldehyde might be affected by the H^+ reduction and hydrogen-hydrogen recombination on the Pt NCs. Adsorption of alcohols and their subsequent oxidation due to trapping of photogenerated holes leads to a decrease in the band bending of TiO_2 NCs. This according to figure 6.3, will lead to an increase in the NW photocurrent, which is observed for the $GaN/(TiO_2-$ Pt) sensors when exposed to methanol and ethanol (figure 10). It is likely that the production of H_2 on Pt is the key for sensing alcohols by $GaN/(TiO_2-Pt)$ sensors. Additionally, H_2 on Pt surface can dissociate and diffuse to the Pt/TiO₂ interface. Atomic hydrogen is shown to produce an interface dipole layer, which reduces the effective work-function of Pt [124]. Effective reduction of Pt workfunction might also reduce the depletion width in TiO_2 , which according to the model in figure 9 would also lead to an increase in the photocurrent, when these sensors are exposed to alcohols. In the presence of hydrogen in nitrogen, the workfunction change of Pt NCs due to hydrogen adsorption is the most likely cause for the sensing behavior of these hybrids.

6.3 Selectivity of $GaN/(TiO_2-Pt)$, GaN/Pt, and GaN/TiO_2 NWNC hybrid sensors

The most significant finding of this study is the change in the selectivity of GaN/TiO_2 hybrid sensors due to addition of Pt NCs. The observed selectivity

behavior of the three hybrids can be qualitatively explained by considering the heat of adsorption of the analytes on TiO_2 and Pt surfaces as seen in table 6.2 and their ionization energies presented in table 6.3.

Table 6.2: Heat of Adsorption for Methanol, Benzene, and Hydrogen on Pt and TiO_2 (Anatase)

Surface	Hydrogen (kJ/mol)	Methanol (kJ/mol)	Benzene (kJ/mol)
TiO2	Negligible [125]	92 [126]	64 [127]
Pt	$100 \ [128]$	48 [129]	117 [130]

Table 6.3: Ionization Energy of the Analytes [1]

Organic Compound	Ionization Energy (eV)
Methanol	10.85
Hydrogen	13.5
Benzene	9.25

The selectivity of the different hybrids can be better explained by answering the following four questions:

1) Why can benzene be detected only by GaN/TiO₂ hybrids, but not by the GaN/(TiO₂-Pt) and GaN/Pt devices?

Looking at table 6.2, benzene has a higher heat of adsorption on Pt than on TiO_2 . Therefore, benzene will preferentially adsorb on Pt in the TiO_2 -Pt cluster. Now, in the absence of Pt, when the benzene is adsorbed on TiO_2 it can interact with the photogenerated charge carriers resulting in the sensing behavior of GaN/TiO₂ devices. However, if benzene is adsorbed on Pt (such as in the case of TiO_2 -Pt and Pt nanoclusters on GaN) then benzene molecules cannot interact with photogenerated charge carriers in TiO_2 , and therefore are ineffective in producing any current modulation in the nanowire.

2) Why is methanol detected by $GaN/(TiO_2-Pt)$ sensors only, and not by GaN/TiO_2 and GaN/Pt sensors?

From table 6.3, methanol (unlike benzene) effectively adsorbs on TiO₂, whether Pt is present or absent (as the heat of adsorption of methanol is higher on TiO₂ than Pt). It is possible that methanol on TiO₂ in the absence of Pt, does not participate in photogenerated carrier trapping as efficiently as benzene and other aromatic compounds on the TiO₂ nanoclusters. Table 6.3 shows the ionization energy of methanol, hydrogen, and benzene. The effectiveness of the process of hole transfer to the adsorbed organic molecules should be related to the compound's ability to donate an electron (i.e. the lower the ionization energy of a compound, the easier for it to donate an electron or capture a hole). However, in the presence of Pt nanoclusters nearby, methanol adsorption on TiO₂ ultimately leads to formation of H⁺ through photo-oxidation of methanol, and eventually H₂, which is the key molecule for sensing of methanol by (TiO₂-Pt) NCs on GaN NW as explained in the previous subsection. Similar argument holds for ethanol sensing by the GaN/(TiO₂-Pt) hybrids.

3) Why is hydrogen detected only by $GaN/(TiO_2-Pt)$ and GaN/Pt hybrids, and not by GaN/TiO_2 NWNC sensors, and why do $GaN/(TiO_2-Pt)$ sensors have higher response to hydrogen than to alcohols?

From table 6.3, hydrogen has negligible heat of adsorption on TiO_2 , thus, GaN/TiO_2 devices are not sensitive to hydrogen. However, in the presence of Pt NCs on TiO_2 , hydrogen can adsorb on the Pt NCs. Once adsorbed, hydrogen can modify the

workfunction of Pt, resulting in a change in the photocurrent through the nanowire. However, this cannot be the only mechanism, as that would imply that GaN/Pt hybrids should be equally sensitive to H_2 . It is likely that when hydrogen is adsorbed on the TiO₂-Pt NC, it can also reduce the TiO₂ surface. Thus, in the presence of only Pt on GaN, workfunction modification of Pt solely produces change in the photocurrent in the NW. However, in the presence of Pt and TiO₂ NCs, hydrogen adsorption leads to the modulation of the photocurrent in GaN NW, through modulation of Pt workfunction together with the change in the depletion layer of the TiO₂ NCs, resulting in a larger change of the photocurrent, thus higher sensitivity. The faster and larger response of GaN/(TiO₂-Pt) towards H₂ compared to the alcohols could be due to the fact that in the case of alcohols, hydrogen is produced after photo-oxidation of the adsorbed alcohols, which is a two-step process with lower yield. In the case of H₂ in nitrogen, there is a direct availability of H₂ molecules.

4) Why are $GaN/(TiO_2-Pt)$ sensors not sensitive to high carbon-containing (C>2) alcohols such as propanol and butanol?

It has been shown that the hydrogen production from the photocatalytic oxidation of alcohols on TiO_2/Pt surface is related to the polarity of the alcohols, i.e., the higher the polarity of the alcohol the greater the yield of photocatalytic hydrogen production [131]. The polarity (Y) is defined as Y = (s - 1)/(s + 2), where 's' is the relative permittivity of the solvent. Table 6.4 lists the polarity of alcohols tested.

The relative difficulty of producing hydrogen from higher carbon-containing alcohols (C > 2) thus might be the cause of the GaN/(TiO₂-Pt) sensor's inability to detect alcohols with C greater than 2. The sensor's greater response to methanol than ethanol (at least for concentrations above 500 ppm) is also consistent with the

Solvent	Polarity (eV)
Methanol	0.91
Ethanol	0.89
n-Propanol	0.86
i-Propanol	0.85
Butanol	0.84

Table 6.4: Solvent Polarity of Various Alcohols Tested

polarities of the alcohols.

6.4 Sensing properties of SnO₂ NP/ GaN NW sensors

The proposed sensing mechanism also explains the response of the SnO_2 -GaN hybrid sensor to the various gases tested in this work. Qualitative representation of band diagram of the SnO_2 -GaN junction is shown in Fig. 6.5. The impact of nanoscale feature sizes on the material properties has not been taken into account.

6.4.1 Response to alcohols

In this section, the interaction of alcohol molecules with SnO_2 surface is breifly reviewed and then an attempt has been made to explain the response of nanoparticle/nanowire sensors for alcohols.

The decomposition of alcohols on metal oxide surfaces in general, and SnO_2 in particular, has been widely studied. The adsorption and decomposition of alcohols on metal oxide surfaces could primarily proceed by i) selective oxidation to aldehyde [132, 133], ii) dehydration to form alkene and water [133], and/or iii) complete oxidation to carbon dioxide and water [134, 135]. Selective oxidation to aldehyde



Figure 6.5: Qualitative band diagram of the SnO_2 -GaN junction. Impact of nanoscale feature size on the material properties has not been considered.

seems to be the favored reaction on SnO_2 surface in the absence of catalytic additives. Thermal desorption spectroscopy of methanol on stoichiometric SnO_2 (110) surface detected formaldehyde and water as the only desorption products besides methanol [136]. A similar mechanism for dissociation of ethanol on the surface of single crystal and polycrystalline SnO_2 (110) to form acetaldehyde and water has been described in Ref. [133]. It has been suggested that gaseous ethanol can undergo a reversible dissociation to an ethoxy group and adsorbed hydrogen as

$$CH_3CH_2OH(gas) \rightarrow CH_3CH_2OH(ads.)$$
 (6.6)

$$CH_3CH_2OH(ads.) \rightarrow CH_3CH_2O(ads.) + H(ads.)$$
 (6.7)

$$CH_3CH_2O(ads.) \rightarrow CH_3CHO(ads.) + H(ads.)$$
 (6.8)

$$CH_3CH_2O(ads.) \rightarrow CH_3CHO(gas) + H(ads.)$$
 (6.9)

$$4H(ads.) + O_2^-(ads.) \to 2H_2O(gas) + e^-$$
 (6.10)

Although the above reactions have been shown to proceed only at higher temperatures, the possibility is that UV excitation in this case promotes these reactions on the device surface even at room temperature. Alternatively, alcohols could be dissociatively adsorbed as alkoxy group and hydrogen (step 6.7 above) without further dissociation to aldehyde at room temperature [137]. Through either route, hydrogen released in steps 6.7, 6.8 or 6.9 can react with the adsorbed oxygen to form water and desorb from the oxide surface as shown in step 6.10.

This alcohol assisted removal of adsorbed oxygen to release free electrons in the SnO_2 nanoparticles manifests itself as the increased conductivity in the nanowire in the presence of alcohol vapors. When tested with various alcohol vapors, the sensor devices show a sensitivity trend in the decreasing order of methanol > ethanol > n-propanol > isopropanol > n-butanol > isobutanol. This is opposite to the behavior observed with the SnO_2 thin films [138], other metal oxide nanostructures such as tungsten oxide (WO₃) nanoplates [98] and ZnO nanowires as seen in this work, i.e. the sensitivity is the highest for n-butanol and the lowest for methanol. At present the reason for the reversal in trend from oxide thin film/nanowire to nanocrystalline coating is not understood.



Figure 6.6: Response of the SnO_2 device to different concentrations of water vapor.

6.4.2 Response to water

Response of the devices towards water was similar to the response towards alcohols, i.e., an increase in photoconductivity was observed with increasing concentration of water vapors as shown in Fig. 6.6. As seen from Fig. 6.6 and Fig 5.13(b) device response to 500 μ mol/mol (ppm) of water is less than the response towards the same concentration of methanol, ethanol and n-propanol but comparable to the response to n-butanol. Therefore, it should be possible for these sensors to detect methanol, ethanol, and n-propanol vapors even under higher humidity conditions.

Various possible mechanisms for interaction of water molecules with SnO_2 surface have been discussed in literature [139]. An increase in surface conductivity in SnO_2 thin films in presence of water has been experimentally proven [140]. The response of SnO_2 nanowires to H_2O at room temperature also shows an increase in conductivity when exposed to water vapors [141]. In this case, as with the SnO_2 nanowire, water could have removed adsorbed oxygen on the surface of the metal oxide nanoparticles leading to an increased concentration of electrons in the nanoparticles and subsequent increase in the photocurrent of GaN NWs.

Chapter 7: -Conclusions and Future Work

Highly selective and sensitive sensors using GaN nanowires decorated with TiO_2 nanoclusters, (TiO_2-Pt) composite nanoclusters and SnO_2 nanoclusters have been demonstrated in this study. The significant features of the sensors are: 1) UV-induced room-temperature sensing as opposed to thermal induced sensing, which promises low-power operation, longer lifetime, and fast on/off capability, 2) selective sensing of aromatic compounds with additional selectivity for methyl group substitution, i.e., these sensors can detect toluene from other aromatic compounds, 3) wide sensing range (50 ppb - 1%), 4) fast response and recovery, and 4) reliable and repeatable operation.

It was shown that the GaN/TiO₂ sensors selectively detected aromatic compounds, such as benzene, toluene, chlorobenzene, ethylbenzene, and xylene. The selective response of GaN nanowire/TiO₂ nanocluster hybrids to the nitroaromatic explosives, including trinitrotoluene (TNT), dinitrotoluene (DNT), nitrotoluene (NT), dinitrobenzene (DNB) and nitrobenzene (NB) at room temperature has also been demonstrated in the present study. A speculation has been made that the photoinduced oxygen desorption and subsequent capture of holes by organic adsorbate molecules on the surface of TiO₂ clusters produces a local-gating effect, which is responsible for the sensing action of the hybrids.

The selectivity of GaN NW based chemical sensors were further tailored by using metal and metal-oxide based multicomponent NCs on GaN NWs. It was found that by adding Pt NCs to GaN/TiO_2 sensors, their sensitivity to the above-mentioned

aromatic compounds can be completely inhibited. However they started responding to hydrogen, methanol, and ethanol. The GaN/Pt NWNCs on the other hand showed response only to hydrogen. The behavior of three different kinds of NWNC hybrid sensor devices, i.e., GaN/(TiO₂-Pt), GaN/TiO₂, and GaN/Pt has been compared. A hybrid GaN nanowire/ SnO₂ nanocluster sensor for selective alcohol sensing at room temperature has also been developed. They showed a different current response for the four organic alcohols, methanol, ethanol, propanol and butanol, and also a unique response for the isomers of propanol and butanol.

This study indicates the potential of metal-oxide and multicomponent NWNC based sensors for developing the next-generation of ultra sensitive and highly selective chemical sensors. Through combinations of metal and metal-oxides available, a library of sensors can be produced, each with precisely tuned selectivity, on a single chip for detecting a wide variety of analytes in many different environments.

7.1 Applications

- Indoor environmental monitoring: The indoor air quality parameters are quite important in places such as hospitals, greenhouses, laboratories. The indoor air quality will directly affect people's working quality and efficiency. Household cleaning products, activities like cooking and tobacco smoking, and equipment like laser printers and computers emit toxic aromatic compounds, alcohols and chlorinated organic compounds that are potential sources of indoor air pollution. The demonstrated sensor technology can be used to build a high performance monitoring system in order to meet the demands of environmental monitoring.
- Hazard Detection and Avoidance: The sensor technology will find application

in places like coal mines, where there is a need for safety of personnel from the hazardous gases like methane. When hazardous material teams respond to a possible terrorist attack or chemical accident, they must carry these kinds of sensors with them to find out exactly what chemical/gas they are dealing with.

- Industrial Monitoring: This sensor technology can be used to provide the most accurate and affordable hydrogen leak detection. They also provide gas monitoring solutions for industrial markets, for example *in-situ* monitoring and characterization of volatile contaminants, vapor detection of gasoline spills and leaks etc.
- Defence: The recent rise in global terrorism made the detection of chemical explosives crucial for homeland security, environmental cleaning and military issues. Developing this sensor technology to selectively detect the explosives will bring down the cost considerably. A chip based on large arrays of nanosensors chemically modified with different binding capabilities using different metal/metal-oxide clusters, in order to detect a whole spectrum of explosive species in parallel, can be created. With several advantages to offer like portability and reliability, the sensing technology has the potential to revolutionize explosive detection.

7.2 Future work

There is a scope for improvement in some of the parameters of the sensor devices presented in this work. At the same time, some of the preliminary findings presented in this work need to be further investigated and verified. Important aspects to be considered in the future work on these sensor devices include:

- Only single-nanowire based devices are studied in this work to better understand the sensing properties. Arrayed architecture could be further developed in order to improve the sensitivity of the devices.
- Room temperature operation of sensors requires greater attention to operation under humidity. Although some measurements for the response of the sensor towards water have been performed, a more reasonable study will be to do measurements under different humidity conditions.
- Though extensive studies have been performed indicating the selectivity of the sensor technology, it should be validated by performing exhaustive analysis in a mixture of possible interfering compounds.
- Effect of UV light intensity on the sensitivity of the alcohol sensors needs to be investigated for a broader intensity range. The current set up limited the maximum intensity to 26 μ W/cm². In the given range, the sensitivity increases with increasing intensity. However the optimal intensity needs to be evaluated as the sensor response is likely to saturate or decrease if the intensity is increased beyond the optimal value.
- Investigation of the effect of oxide quality on sensing behavior could be a useful study to perform. Oxygen deficient vs. oxygen rich oxide, dense vs. sparse deposition of oxide nanoparticles could be important control parameters for the sensor response characteristics.
- Commonly encountered challenges like drift current and aging effects need to be studied and analyzed for these sensor devices.



Appendix A: - Mask Layout

Figure A.1: Complete layout of the mask layout used for developing gas sensing devices. Scale bar units are in mm.



Figure A.2: Geometry of few electrode patterns in the mask. Scale bar units are in $\mu \mathrm{m}.$

Appendix B: - Characterization tools

This appendix gives a brief description of the characterization tools which were used to study the morphology and microstructure of the nanowire-nanocluster sensors.

B.1 Scanning electron microscopy

SEM is a method for high-resolution imaging of surfaces. The microscope uses electrons in instead of light to form an image. Advantages of SEM microscopy include i) large depth of field allows a large area of sample to be in focus at one time, ii) high resolution, and iii) easy preparation of sample as most SEMs only require the sample to be conductive.

The SEM generates a beam of incident electrons in an electron column above the sample chamber. The electrons are produced by a thermal emission source, such as a heated tungsten filament, or by a field emission cathode. The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of the column direct and position the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging.

The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the samples surface and near-surface material. Emitted lower-energy electrons resulting from inelastic scattering are called secondary electrons. To create an SEM image, the incident electron beam is scanned in a raster pattern across the sample's surface. The emitted electrons are detected for each position in the scanned area by an electron detector. The intensity of the



Figure B.1: Schematic representation of electron-specimen interaction in SEM

emitted electron signal is displayed as brightness on a cathode ray tube (CRT). By synchronizing the CRT scan to that of the scan of the incident electron beam, the CRT display represents the morphology of the sample surface area scanned by the beam. Magnification of the CRT image is the ratio of the image display size to the sample area scanned by the electron beam.

B.2 Transmission electron microscopy

TEM is also an electron microscope which uses electron beam instead of light to form an image. The transmission electron microscope uses a high energy electron



Figure B.2: Schematic representation of a transmission electron microscope.

beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.0025 nm. However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 0.1-0.2 nm.

Because even for very thin samples one is looking through many atoms, one does not usually see individual atoms. Rather the high resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution. The brightfield/darkfield imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material. Finally the microscope is equipped with a special imaging lens allowing for the observation of micromagnetic domain structures in a field-free environment.

B.3 X-ray diffraction

X-ray diffraction is one of the most commonly used characterization techniques to study the crystal structure of materials. The wavelength of X-rays is comparable with interatomic spacing in materials; therefore, a wealth of information can be gained by studying the interaction of X-rays with materials. X-ray (electron, neutron, etc.) diffraction is based on Braggs law (eqn. 2.1) which relates the interatomic spacing, d, with the x-ray wavelength, λ and incident angle, θ .

$$n\lambda = 2d\sin\theta \tag{2.1}$$

XRD measures the diffraction pattern of the scattered X-rays after collision of X-ray photons with the sample. If the atoms in the sample are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring diffraction pattern therefore allows us to deduce the distribution of atoms in a material.

B.4 Electron backscattered diffraction

EBSD operates by arranging a flat, highly polished (or as-deposited thin film) sample at a shallow angle, usually 20°, to the incident electron beam. Electron diffraction occurs from the incident beam point on the sample surface. Constructive and destructive interference occurs between the back scattered electrons which are produced when the primary beam interacts with the crystal lattice. Diffraction pattern can be seen on a phosphor screen placed in the path of diffracted electrons. Specialized computer software analyzes the electron backscatter pattern (EBSP). With a *priori* information about the crystal phases, the software identifies the best fit for the sample.

List of Relevant Publications

 G.S Aluri, A. Motayed, K. Bertness, N. Sanford, V. Oleshko, A.Davydov, M.V. Rao, Highly selective GaN-nanowire/TiO₂ nanocluster hybrid sensors for detection of benzene and related environmental pollutants, Nanotechnology 22, 295503, (2011).

2) G.S Aluri, A Motayed, A.V. Davydov, V. Oleshko, K. Bertness, N. Sanford and M.V. Rao, "GaN-nanowire/ TiO₂-nanocluster hybrid sensors for detection of Benzene and related aromatic compounds", Proc. SPIE 8024, 80240M (2011).

3) G.S Aluri, A. Motayed, K. Bertness, N. Sanford, V. Oleshko, A.Davydov, M.V. Rao, Methanol, Ethanol, and Hydrogen Sensing using Metal-Oxide and Metal (TiO₂-Pt) Composite Nanoclusters on GaN Nanowires: A New Route towards Tailoring the Selectivity of Nanowire/Nanocluster Chemical Sensors, Nanotechnology 23, 17550, (2012).

4) R. Bajpai, A Motayed, A.V. Davydov, V. Oleshko, G.S Aluri, K. Bertness, M.V. Rao, M. E. Zaghloul, SnO₂ nanocluster coated GaN nanowire hybrid sensor for selective alcohol sensing at room temperature, Sensors and Actuators (in press).

5) G.S Aluri, A. Motayed, K. Bertness, N. Sanford, V. Oleshko, A.Davydov, M.V. Rao, Nano-sensors for trace detection of Nitroaromatic Explosive compounds using Nanowire-Nanocluster hybrids (in preparation).

Other Publications

6) G.S Aluri, M. Gowda, N.A. Mahadik, S.G. Sundaresan, M.V. Rao, J.A. Schreifels, J.A. Freitas, S.B. Jr, Qadri, Y-L Tian, Microwave annealing of Mg-implanted and in situ Be-doped GaN, J. Appl. Phys. 108, 083103 (2010)

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Curriculum Vitae

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