
Group III-V Nanostructures Application in Gas Sensing

Sanele G. Nyembe

(397091)

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Supervisors: **Prof N. Moloto (Wits) and Dr L. Sikhwivhilu (Mintek)**

Co-supervisor: **Dr R. Harris (UFS)**

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DECLARATION

I declare that this thesis is my own original work under the supervision of Professor Nosipho Moloto (University of Witwatersrand), Dr Lucky Sikhwivhilu (Mintek) and Dr Richard Harris (University of Free State). It is being submitted for the degree of doctor of philosophy to the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination in any other university.

Sanele G. Nyembe

Signature: _____

Date: ____/____/ 2018

ABSTRACT

The advent of nanoscience and nanotechnology has made it possible to control several properties such as material shape, size and stability. However, different production approaches are often required. Engineered surfaces with tailor-made properties such as large surface area or specific reactivity are used routinely in a range of applications such as in fuel cells, catalysis, etc. Nanomaterials with unique morphologies have been developed and used in fields such as electronic device manufacture, chemistry and engineering.

Synthesis of gold icosahedral (I_h) and decahedral (D_h) nanostructures was successfully achieved through a two-step heterogeneous nucleation process. Citrate stabilised seeds were used to grow these nanostructures. Cetyltrimethylammonium bromide (CTAB) was used to promote fast growth of Au nanostructure along the [111] crystal lattice plane. D_h and I_h nanostructures are known to be thermodynamically unfavourable above size of 5 nm. Successful growth of such nanostructures above this critical size limit was explained in terms growth kinetics. Gold nanostructures were found to have an average particle size of 50 nm and a narrow size distribution range of 45 nm to 55 nm. The seeds were fast-handled during growth to enhance the formation of these nanostructures. In-depth characterisation of these nanostructures confirmed that they formed via crystal twinning mechanism.

Synthesis of gold nanostructures with different sizes was achieved through a three-step heterogeneous nucleation process. Different types of seeds were prepared using different stabilizers (Citrate and CTAB). Citrate and CTAB stabilized seeds were used to grow Au nanostructures separately. The CTAB stabilized seeds showed polydispersity, suggesting the presence of various shapes. These seeds produced agglomerated particles of various shapes with a wide particle diameter distribution ranging from 50 nm to 200 nm. The triangular Au nanostructures present in the mixture had a 3 dimensional morphology (i.e. pyramid shape) as confirmed by atomic force microscopy (AFM). The citrate stabilized seeds were monodisperse and they yielded well dispersed Au nanostructures with uniform morphologies. These Au nanostructures had an average particle size of 50 nm and a narrow size distribution range of 45 nm to 55 nm.

Laser assisted synthesis of silicon nanowires (SiNWs) was achieved through the use of gold and nickel nanoparticles as catalysts. The diameter of the resulting SiNWs was found to be dependent on that of the catalyst. The gold catalysed silicon nanowires were unevenly curved and branched owing to the high kinetic energy possessed by gold nanoparticles (AuNPs) at relatively high processing temperature. The use of nickel as catalyst resulted in the formation of several SiNWs on a single nickel catalyst due to interconnection of the nickel metal particles at processing temperature. The morphology of SiNWs catalysed by both nickel and gold was controlled by optimising the laser energy during ablation.

Indium phosphide nanowires (InPNWs) with an average diameter of 87 nm were successfully synthesized through thermal chemical vapour deposition (CVD) method. The smooth surface nanowires showed a relatively narrow size distribution of 70 nm to 105 nm. Temperature programmed desorption (TPD) was used to study the thermodynamic behaviour of gas desorption. The study revealed that gaseous CO and CH₄ molecules bind to InPNW surface through chemical and physical adsorption. Redhead method was used to estimate the enthalpy energy of desorption for CO and CH₄ to be 142 kJ/mol and 38 kJ/mol. The sorption temperature ranges were found to be 220 °C to 260 °C for CO and -50 °C to -20 °C for CH₄. InPNWs were used to fabricate a gas sensor electronic device and were tested for performance. The device showed a quick response time of 29.19 s for CO at 250 °C.

Indium arsenide nanowires (InAsNWs) with an average diameter of 45 nm were successfully synthesized using homogeneous catalysis approach and chemical vapour deposition method. Successful synthesis of InAsNWs was achieved at a temperature of 700 °C suggesting that solution-liquid-solid growth mechanism was involved. Synthesis conditions were optimised to minimise InAsNWs polytypism and stacking faults. The results showed that InAsNWs have significant adsorption sites and affinity for CO and H₂S gases due to the formation of electron accumulating surface. The calculation of enthalpy energy of desorption revealed that interaction of InAsNWs and CO was through physisorption. InAsNWs showed a response time of 72s for CO at 250 °C. Characterization of the nanostructures was carried out using high resolution transmission electron microscope (HRTEM), Raman spectroscopy, high resolution scanning electron microscope (HRSEM), UV-Vis spectrometer, X-ray diffractometer (XRD), temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

KEYWORDS

Gold nanostructures, Icosahedron, Monodispersed, Twinning mechanism, Stabilizing agents, Silicon nanowires, Vapour-liquid-solid growth mechanism, Laser ablation, Indium phosphide, Chemical vapour deposition, Temperature Programmed Desorption (TPD), Diffuse Reflectance Infrared Fourier transform Spectroscopy (DRIFTS), Gas sensing, Analyte gas, Enthalpy energy, Desorption, Response time.

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This dissertation is a huge milestone for me as a young scientist. Starting this PhD project, I always reminded myself of a quote by Abraham Lincoln that states “*If I had nine hours to chop down a tree, I’d spend the first six sharpening my axe*”. It inspired a new level of planning that proved to be the key element for my success. There were lots of challenges throughout the completion of this study and I have the following people to thank for the success of my journey:

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DEDICATIONS

All glory goes to God for guidance throughout my life. I would like to dedicate this thesis to the following people:

- My parents (Mrs Thandie Nyembe and Mr Petros Nyembe)
- My siblings (Winnie, Thamie, Zama, Siyabonga Nyembe)
- My late little brother (*Siphesihle Nyembe*)
- My nephew (Mthokozisi Gumede)
- My child and fiancée (Sazi Sphehile Nyembe and Zinhle Pearl Gasa)

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LIST OF PUBLICATIONS/PRESENTATIONS/RESEARCH VISITS

Publications Emanating from this Thesis:

- **S. Nyembe**, S. Mpelane, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, Platonic Gold Nanocrystals: Icosahedron and Decahedron Nanostructures through Twinning Mechanism, *Journal of Nanoscience and Nanotechnology*, 16 (9), **2016**, 9832-9837. **(Published)**
 - **S. Nyembe**, S. Mpelane, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, The Effects of Gold Seeds Stabilizing Agent on Gold Nanostructures, *Materials Today Conference Proceedings 2*, **2015**, 4149-4157. **(Published)**
 - **S. Nyembe**, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, Laser Assisted Catalytic Growth of Silicon Nanowires using Gold and Nickel Catalysts. **(Submitted for Review)**
 - **S. Nyembe**, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, Crystal Growth and Electron Transport of Indium Phosphide Nanowires Supported by Monte Carlo Simulation. **(Manuscript prepared)**
 - **S. Nyembe**, P. Shumbula, R. Harris, N. Moloto, T. Ntho, L. Sikhwivhilu, Adsorption of Methane and Carbon Monoxide onto Indium Phosphide Nanowires: TPD and DRIFTS Study **(Manuscript prepared)**.
 - **S. Nyembe**, B. Mwakikunga, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, Indium Phosphide Nanowires Gas Sensing Properties. **(Manuscript prepared)**.
-

Additional Publications:

- P. Shumbula, R. Harris, **S. Nyembe**, F. Keter, L. Sikhwivhilu, R. Tshikhudo, Cytotoxicity Effects of Citrate, Glucose and Cetyltrimethyl Ammonium Chloride-Capped Silver Nanoparticles in Lung Epithelial Carcinoma Cells (A549), Materials Today Conference Proceedings 2, **2015**, 4118-4124. **(Published)**
- T. Xaba, P. Morgan Shumbula, **S. Nyembe** and P. Tetyana, Bis(N-benzyl-salicydenaminato) copper (II) as a precursor for the synthesis of copper oxides nanoparticles and thin films through thermal decomposition technique, Journal of Nanotechnology, **2018**. **(Submitted for Review)**
- **S. Nyembe**, P. Shumbula, R. Harris, N. Moloto, L. Sikhwivhilu, Gold Nanowires Surface-Enhanced Raman Spectroscopy Properties in Comparison with Different Sizes of Spherical Gold Nanoparticles. **(Manuscript prepared)**.

Publications in a form of Mintek Reports:

- **S. Nyembe**, N. Moloto, L. Sikhwivhilu, Synthesis of Semiconducting Nanowires and Fabrication of Electronic Device (Internal Report # 42451), **30 September 2016**.
 - **S. Nyembe**, N. Moloto, L. Sikhwivhilu, Adsorption of methane and carbon monoxide onto Indium Phosphide Nanowires: TPD and DRIFTS study (Internal Report # 42 673), **31 March 2017**.
-

Oral Presentations:

Local

- MAM-14 International Symposium on Macro- and Supramolecular Architectures and Materials (Emperors Palace, Johannesburg, South Africa) on **23-27 November 2014**: Gold Icosahedrons and Decahedrons Nanostructures formed through Twinning Mechanism.
- University of Witwatersrand-Vaal University of Technology Student's Seminar, Chalsty Audio Visual Room Law Building, West Campus on **11 September 2015**: Synthesis of Indium Phosphide Nanowires through Chemical Vapour Deposition.
- 42nd National Convention South African Chemical Institute, Elangeni, Durban, South Africa on **29 November - 04 December 2015**: Growth of Indium Phosphide Nanowires through Solution-Liquid-Solid.
- 3rd International "Nano-Carbon" Workshop South Africa, Senate Room Senate House, University of Witwatersrand on **14-15 January 2016**: Crystal growth and Properties of Indium Phosphide Nanowires.
- Nanotechnology Innovation Centre (NIC) Group Meeting, Mintek/Advanced Material Division (AMD) Meeting Room, Randburg on **29 January 2016**: Synthesis and Characterisation of Indium Phosphide Nanowires.
- 6th International Conference on Nanoscience and Nanotechnology in Africa (Nano Africa 2016), Thamsanqa Kambule Auditorium, University of South Africa, Science Campus, Johannesburg on **03-06 April 2016**: Sorption of Carbon Monoxide and Methane Gases on the Surface of Indium Phosphide Nanowires.
- 7th World Nano Conference, Double Tree Upper Eastside by Hilton, Cape Town, South Africa on **21-22 June 2016**: Gas Sensing Properties of Indium Phosphide Nanowires.

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- 6th Annual Gauteng Nanosciences Young Researchers Symposium (NYRS), Mintek Auditorium on **18 November 2016**: Interaction of CO with Indium Phosphide Nanowires: optimisation of a Gas Sensor.
 - Advanced Material Division, Mintek level 14 Auditorium on **8 February 2017**: Indium Phosphide Nanowires and Carbon Monoxide Interaction.
 - University of Cape Town on **2-3 May 2017**: Adsorption Studies of Indium Phosphide Nanowires: TPD and DRIFTS.
-

Poster Presentations:

Local

- Nanotechnology Innovation Centre Workshop 2017, Medical Research Council, Cape Town, **24-26 January 2017**: Gas Sensing Potential of Indium Phosphide Nanowires.

International

- Tech-Connect World Innovation Conference and Expo 2017, Washington DC, **USA, 14-17 May 2017**. Indium Phosphide Nanowires Application in Gas Sensing.
-

Local Research Visits and Summer School Attendance:

- **Council of Scientific and Industrial Research (CSIR), Department of Advanced Material for Device Applications, 23-27 April 2016.**

The visit to the CSIR at the advanced material for device application was to conduct gas sensing analysis of nanowires. The gas sensing tests were done using various analyte gases such as H₂S, NO₂, CO, CH₄ and H₂. The results are included as part of this thesis.

-
- **University of Cape Town, Department of Physics, Nano Electronic Laboratory, 13-17 June 2016.**

The visit to the nano-electronics laboratory at the Physics department at UCT was for indium phosphide nanowire single nanowire electronic device fabrication and for electron mobility measurements. Electrical properties such as current-voltage (I-V) was measured successfully and it is included as part of this thesis.

- **The 4th South African Nanoscience and Nanotechnology Summer School, North West University – Potchefstroom, 04 – 09 December 2016.**

The vision of the school was to bring together experts in the nanoscience/nanotechnology field (local and international) to present courses, covering topics on introduction health and safety risks presented by nanotechnology. The research, hazard identification, exposure assessment, risk assessment and challenges of nano HSE were explored. The summer school was important because this project involved a lot of material in a nanoscale range.

Awards and Recognitions:

- **Best Oral Presentation, PhD 1st Prize**

6th Annual Gauteng Nanosciences Young Researchers Symposium (NYRS) held at Mintek Auditorium on the **18th of November 2016**. The presentation was titled: Interaction of CO with Indium Phosphide Nanowires: Optimisation of a Gas Sensor.

- **MiniMag Magazine Career Profiling:**

Minimag a national kid's magazine profiled my career as the young scientist in nanotechnology in their August 2016 issue, vol. 21, number 12 (252), page 12.

Trade Secrets/Discoveries Filed:

➤ **Nanotechnology Enabled Soap**

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LIST OF ACRONYMS

InPNWs	Indium Phosphide Nanowires
InAsNWs	Indium Arsenide Nanowires
AuNPs	Gold Nanoparticles
DEP	Di-electrophoresis
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
VLS	Vapour-Liquid-Solid
SiNWs	Silicon Nanowires
EBL	Electron Beam Lithography
CO	Carbon Monoxide
XRD	X-Ray Diffraction
SLS	Solid-Liquid-Solution
FCC	Face Centered Cubic
TPD	Temperature Programmed Desorption
AFM	Atom Force Microscope
MEMS	Micro-Electro-Mechanical-Systems
DOS	Density of States
LA	Laser Ablation

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General Introduction

Over the years mining in South Africa directly contributed to the establishment of the Johannesburg Stock Exchange in the late 19th century, and today it still accounts for a third of its market capitalisation. It is clear how much mining in South Africa has shaped the country politically, culturally, and economically. However, the growing number of fatalities among miners caused by toxic gases puts pressure on the mining industry [1]. As such innovative approaches are required to improve underground miner's health. Toxic gases are very often released in underground mines and cannot easily be detected by human senses such as nose detection. Concentration of mine gases such as carbon monoxide, methane, nitrogen oxide, etc. found at any time and location may vary due to different factors like diffusion, turbulent dispersion, and leakage in subsurface ventilation systems [2-4]. Therefore, it is necessary to deploy sensors to monitor and measure toxic and flammable gas concentration levels in subsurface environment for the safety of underground miners as well as mines. The development of technologies that can detect very low concentration (parts per billion) of noxious gases along with improved ventilation could effectively improve safety and unhealthy air quality in mines.

Today there are various nanotechnology-enabled gas sensors and most currently use active materials for solid state gas sensors which are typically polycrystalline sintered metal oxide semiconductor such as zinc oxide (ZnO), tin oxide (SnO₂), etc. [5]. However, high operational temperatures lead to metal oxide semiconductor grain growth thereby compromising response time of the gas sensor [1]. Novel semiconductor material based devices are ideal for next generation of sensors for long term stability, high surface to volume ratio, better gas selectivity and self-heating capacity. So, the challenge is to fabricate nanotechnology-based sensor device with improved sensitivity, reduced power consumption and relatively lower limit of detection as well as relatively lower operating temperature.

Gas sensors can be grouped based on operation mechanism and material used for fabrication. Operation mechanism and the choice of material is based on the chemical changes being monitored by the sensor which could be optical absorption, modulation of the field, electrical current, etc. Based on technology the global gas sensor market can be classified as, semiconductor, electrochemical, solid state, photosonication detector (PID), infrared, catalytic and others [6]. However, based on the end-users perspective the global gas sensor market can be broadly classified as medical, environmental, building attenuation, domestic, automotive, petrochemical, industrial etc. For all this, industrial segment accounts for the largest usage of gas sensors.

Semiconductor nanowire based devices are ideal for next generation of sensors due to long term stability, high surface to volume ratio, better gas selectivity, and self-heating capacity. Semiconductor nanomaterials are ideal candidates for fabrication of sensor devices with improved sensitivity, low power consumption, lower limit of detection. V. Sysoev *et al*, reported that nanowire based gas sensors have relatively better sensing reproducibility compared to SnO₂ thin film based sensors [6-7]. Elongated nanomaterials (i.e. nanowires) morphology provides electrical conductivity and high surface area to volume ratio which are important in semiconductor based gas sensors [8-10]. Nanomaterials such as carbon nanotubes, metal oxide nanowires lead to improved gas selectivity and smaller devices [11].

The aim of this work was to improve response time and sensitivity of semiconductor based gas sensor. The approach was to use semiconductor nanowires such as Si, InP and InAs as active gas sensing material. These semiconductors have relatively small tuneable band gaps and high electron mobility compared to most metal oxides [12-13], which has a potential to improve response time in gas sensors. Nanowires such as Si, InP and InAs were grown in the presence of stable catalyst such as gold nanoparticles and nickel using CVD. Fabrication of nanowire based sensor device will be explained. The sensing performance of InP and InAs was compared to other materials.

1.1 Brief Description of the Thesis

Background of the topics covered in the thesis are explained in **Chapter 2**. The instruments used for the synthesis, characterisation and analysis of all the samples are shown and explained in **Chapter 3**. The effects of stabilizing agent and its concentration on the size and shape of gold nanoparticles is explained in **Chapter 4 and 5**. The synthesis of silicon nanowires in the presence of metal catalysts through laser ablation and the relationship between the nature and characteristic of the catalyst on the effect of nanowires is explained in **Chapter 6**. The relationship between gas adsorption studies i.e. TPD and DRIFTS in predicting gas sensing capabilities of semiconductor nanowires is described in **Chapter 7 and 8**. General conclusions of the project and recommendations for future work are described in **Chapter 9**.

1.2 Problem Statement

Metal oxide semiconductors thin film based gas sensors have high response time for toxic gases. Hence, efforts have been made to improve sensor performance while keeping production cost low. Exploration of new material with tuneable properties may be an advantage in improving current gas sensor performance.

1.3 Motivation

Group III-V semiconductors cover a wide band gap and relatively high electron mobility which can be engineered by the manipulation of size, shape and doping. Incorporating these materials in semiconductor based sensing device presents possibilities of a better sensor performance.

1.4 Aims and Objectives

The aim of the project was to synthesize and characterise Si, InP and InAs nanowires and use them as active materials in a gas sensor device. In order to fulfil the above aim, the following objectives were identified:

-
- Synthesis and characterisation of colloidal gold nanoparticles with different sizes and shapes were used as catalysts for growing semiconductor nanowires.
 - Synthesis and characterisation of semiconductor nanowires using a metal catalyst.
 - Semiconductor based sensor device was fabricated and sensor performance was measured.

1.5 References

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Literature Review

2.1 Introduction

Sensors have become indispensable to various industries, as they provide important information across a wide range of parameters, including temperature, position, chemical, pressure, force, etc. and can affect products, processes and systems [1-7]. Furthermore, image sensors have increasingly experienced the highest growth because of their increased use in smartphones and other portable devices [8-9]. However, the biosensors and chemical sensors category is considered the second-largest and fastest segment of the market and is expected to see rapid growth [10]. This rapid growth is catapulted by the increased use for medical purposes, as well as the rising number of threats of terrorist attacks at key industrial facilities such as chemical plants and mines. Inevitably, technological advances in electronic control systems, decreasing cost expectation, miniaturisation and improved communication capabilities are expected to significantly drive growth across all segments of the sensor market for the foreseeable future [11-12]. For this reason the semiconductor industry is attempting to recapture its intensive capital investment by developing sensor solution to address large-scale, high-volume consumer-related applications [13].

Technological advancement and needs for chemical (solid, gas or liquid) and biological species detection are giving rise to continuous research and development in physico-chemistry and biology [14-15]. Significant and constant progress is being made, especially in the theoretical and technological aspects concerning development of chemical sensors and biosensors [10]. So, the development of a chemical sensor that can provide reliable quantitative and selective measurement of the analyte even in small concentrations and for use in real-time monitoring is desirable. A good sensor must possess the following characteristics: accuracy, sensitivity, selectivity, repeatability and reproducibility, stability, short response time and recovery time, low operating temperatures, etc. [16-25] However, in order to achieve all these characteristics the choice of sensing material and its physico-chemical properties are essential [14]. For this reason semiconducting metal oxides such as ZrO, TiO₂, ZnO, etc. have been widely used and investigated in the detection of gases [26-

29]. However, before the advent of fabrication techniques for nanowires, various nanostructures of different semiconductors were preferred material for gas detection [30-37].

Gaining traction in solid-state sensing technology is the development of nanomaterials and nanostructures with novel functionalities and innovative properties at the nanoscale for high-performance chemical sensing [27, 33]. The actual stake of the nanotechnology has reached mature advancements for the nanomaterials processing including functionalisation, nanocomposites, hybridisation of materials, nanoparticles, nanowires, nanotubes, nanofibers, nanobelts and sensing nanodevices to fabricate chemical sensors with tailored characteristics and fine-tuned properties at the nanoscale level [38-41]. However, the most common gas or chemical sensing principle is underpinned by the adsorption and desorption characteristics of gas molecules on the sensing materials - sensitivity can be greatly enhanced [40-41].

Recent developments in nanoscience and nanotechnology have created great potential to build highly sensitive, low cost, portable sensors with low power consumption. The very large surface area to volume ratio, unique morphologies such as nanotubes, nanowires, nanofibers and nanoparticles are ideal for gas molecules adsorption and storage [42-46]. However, in order to control the material geometry, morphology and properties a good choice of material and preparation method is pivotal [47-48].

This chapter is divided into three main sections (i) *solid catalysts*, (ii) *semiconductor nanowires* and (iii) *electronic device fabrication*.

2.2 Solid Catalysts

A catalyst is a substance that increases the rate at which a chemical system approaches equilibrium without itself undergoing any permanent chemical change. Catalyst increases the efficiency of a chemical reaction in order to occur at milder conditions than would otherwise be possible [49-50]. When the catalyst and reactants or products are in the same phase, the catalyst is considered a *homogeneous* catalyst. A *heterogeneous* catalyst on the other hand is in different phase to the reactants and products [51-52]. The most common catalysts are the enzymes from most living organisms; they are considered the most important biological catalysts because of their functions such as decomposition of food [53].

Catalysis is undoubtedly the most relevant process in the production of most industrial chemicals notably in material science (i.e. Haber process, catalytic cracking of gas oil), organometallic chemistry (i.e. ferrocene for production of carbon nanotubes) and environmental science such as the catalytic convertors in cars [54-58].

In practice, catalysts generally react with one or more reactants to form an intermediate product that subsequently give the final reaction product, in the process regenerating the catalyst [55-57]. However, the regenerated catalyst can mix with the reaction product homogeneously thereby contaminating the product [55-58]. For this reason, heterogeneous catalysts are generally preferred over homogeneous catalysts because they could be easily separated and removed at the end of the reaction [51-52]. Furthermore, P.A Russo et al reported that solid catalysts at nanoscale are more effective and can radically alter their performance due to their relatively larger surface area when compared to their bulk counterparts [59-61]. G. Centi et al established that for well-defined nanocrystals the exposure of specific facets can increase or decrease surface reactivity and metal-support interaction (for supported metal nanoparticles), subsequently affecting catalytic reactions [62-64].

2.2.1 Synthesis of Nanoparticles

Metal nanoparticles-based catalysts can significantly improve catalytic activity because they have higher surface area [65-66]. Since nanoparticles have improved properties compared to their bulk counterparts, many transition metals, transition metal oxides are increasingly used in catalysis [67-70]. In principle, the most important factor in determining catalytic activity and efficiency in heterogeneous catalysis is the sufficiently larger surface area, which is often achieved by the use of either nanoparticles or granular particles with porous characteristic [71-72]. However, controlled synthesis of nanoparticles can be a challenging task. In recent past, several methods have been developed to control the formation of uniform particle size distribution at nanoscale [73-78]. As such, nanoparticle-based catalysts could be monodisperse, polydisperse or aggregates. Nanoparticle size and molecular structure are two properties that can be controlled using nanotechnology [78].

The role of nanoparticles in catalytic processes is fundamentally important from the environmental point of view because of their relevant characteristics such as activity, selectivity, durability and recoverability [79-80]. As a result of this, understanding the relationship between the structure and composition of catalysts surface and catalytic properties has fundamental importance in the application of nanoparticles [70-72, 79].

The major advantage of using nanoparticle-based catalyst is the active surface which is known to increase when the catalysts size is reduced or decreases [59-61]. Thus, the smaller particles means greater surface to volume ratio and reaction efficiently and consequently the required amount of catalyst for reaction decreases [60]. In order to understand the effects of surface energy on the morphology of nanoparticles, the thermodynamics of nanoparticle formation becomes important.

2.2.1.1 Importance of Thermodynamics in Nanoparticle Formation

The thermodynamics of nanoparticles formation is important because it allows design of nanoparticles with unique properties. Thermodynamics of nanoparticles is affected by surface and interface of nanoparticles. O'Connor et al stipulated that theoretically, the synthesis of crystalline nanoparticles in solution phase involves three steps namely: (i) nucleation, (ii) nuclei growth and (iii) termination of the growth and stabilisation [81-82]. Accomplishing temporal separation of the nucleation and growth steps leads to a controllable nanoparticles size and shape. Temporal manipulation of nucleation and growth steps can be achieved by reaction conditions such as temperature and concentration gradients. High surface energy nanoparticles are thermodynamically unstable hence agglomeration is inevitable to minimise the surface energy. Steric and electrochemical repulsions from stabilisers are important in controlling the agglomeration process [83-86]. Amongst metal nanoparticle, Au nanocatalysts are advantageous because of great stability and strong interaction with stabilisers such as citrate and CTAB.

2.2.2 Synthesis of Gold Nanoparticles

The most common method of synthesizing gold nanoparticles was first reported in 1951 by J. Turkevich et al [87-88]. They reported on the reduction of gold ions in aqueous solution using a reducing agent in the presence of stabiliser. Factors including temperature, concentration, and stirring rate were reported to be fundamentally important for morphology control. Au nanoparticles produced via this method tend to have spherical shape and are typically stable. In principle, these nanoparticles can have diameter ranging from 8 nm to 73 nm depending on the concentration of citrate used. J. Gao et al further modified this method by using CTAB as stabilizer resulting in the formation of particles with unique morphology such as cubes, triangles, hexagons, etc. [89-91].

2.3 Semiconductor Nanowires

Industry report released in 2016 by British Broadcasting Corporation (BBC) shows that the semiconductor nanowire-based devices such as solar cells, capacitors, etc. will rapidly increase to an estimated value of \$3.4 billion by year 2022 [100]. On the other hand big cooperation such as Intel, IBM and Samsung continue to take advantage and dominate intellectual property (IP) protection in the field of semiconductor-based devices. The use of nanowire-based devices holds promise for functional devices that could improve safety and quality of life in general [100-101].

Nanowire is a cylindrical one-dimensional nanostructure that exhibits an aspect ratio greater than 1000 with the diameter confined in the nanometer range or less and unconfined length [102-105]. Amongst various types of nanowires semiconductor nanowires find application in electronics because of relative ease in controlling the flow of electrons more efficiently when compared to superconductor, insulator and molecular nanowires, [106-111]. This is an important characteristic for the development of functional electronics [112-113].

Of all one-dimensional nanostructures nanowires and nanotubes are, by far, more attractive for application than rest (i.e. nanofibers, nanorods, nanobelts, etc.) owing to their relatively larger surface area [114-120]. However, nanowires exhibit superior and interesting electrical transport properties that are not commonly observed in bulk material [121-125]. This is

because in nanowires or quantum wires electrons could be confined laterally leading to occupation of discrete energy levels that are different from the energy bands found in bulk materials [125-126]. Inevitably, low electron density and low effective mass means that quantized conductivity is more easily observed in semiconductor materials (i.e. Si, GaN, etc.) [127-130]. For this reason, synthesis of high quality semiconductor nanowires is imperative and there are several methods used to fabricate these nanostructures with sub-100 nm size range [131-133].

2.3.1 Metal Catalytic Growth and other Methods

The metal catalytic growth method relies on the use of metal nanocatalyst and can produce non –agglomerated or free-standing crystalline nanowires of semiconductor and metal oxide materials with controlled nucleation sites and diameters from pre-fabricated metal catalysts [134-142].

The constantly growing interest in studying fabrication of semiconductor nanowires has led, more recently, to the development of various new techniques. These include techniques such as laser assisted chemical vapour deposition (CVD), thermal CVD, metal-catalysed molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE) [143-150]. The availability of several techniques to fabricate one-dimensional nanostructures means there are tons of these nanostructures produced every day. However, the accuracy and precision to fabricate desired one-dimensional nanomaterials with tailored atomic structures and integration of functional nanostructures into devices are still challenging issues [151-152]. Currently, metal catalysed MBE and CBE have been used to produce high quality and very thin nanowire structures. These techniques facilitate better control levels over atomic structures, chemical composition, defects, doping state, etc. [153-160].

2.4 Semiconductor Nanowire-based Electronic Device

Semiconductor nanowires are known for their unique properties to transport electrons and electron-holes [161-163]. As such they are considered as the building blocks for nanoscale electronics that can be assembled without the need to utilise complex and expensive fabrication infrastructure such as lithography [124, 164]. Different types of semiconductor nanodevice have been fabricated using various nanostructures and these include hybrid

semiconductor devices, one-dimensional devices and advanced molecular devices. However, devices that utilise silicon and non-silicon materials are known to offer high speeds and excellent performance [165-170]. In order to continuously and incrementally improve device performance researchers now make use of a core-shell structures of nanowires leading to confinement of electrons and electron-holes into a small space. This effectively allows electrons to pass through the nanowires quickly - a phenomenon necessary for speed improvements [171-175].

2.4.1 Field-Effect Transistors

Amongst different semiconductor devices, field-effect transistor (FET) has been widely studied and as such they are considered as promising candidate for applications in spintronics, DNA and protein detection, etc. [176-177]. FET uses electronic field to control the electronic behaviour of the device [178-179]. Nanowire-based FET has become a device of note and is typically used in the development of high performance, multi-nanowire devices and circuits on nanocrystalline substrates and arrays of single nanowire FET for chemical sensing [180-182]. Silicon nanowires have been extensively used to assemble these types of devices and they are highly reproducible. For this reason successful attempts have been made to fabricate sensors for ultrasensitive detection of biological and chemical species. These species tend to bind to the surface of nanowire-based FET leading to the depletion or accumulation of carriers and subsequent changes in the conductance of nanowires [182-185]. This implies that the high surface area and high performance of nanowires-based FET could result in high sensitivity [180, 182].

2.4.2 Light Emitting Diodes

Light emitting diodes (LEDs) are a p-n junction semiconductor light devices that emit light when activated [186-188]. The concept of flexible LEDs has become topical especially in respect to various applications in displays, wearable electronic devices, etc. [189]. The light emitting diodes use organic materials integrated on light-weight and flexible plastic structures [190-192]. Flexible organic LEDs are very useful for the development of flexible devices owing to their flexibility, relatively ease of processing, low cost and compatibility with other

flexible substrates [190-193]. The use of nanowires in these light emitting devices facilitates light extraction because of their wave guiding properties [194-195].

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Experimental Methods and Characterisation Techniques

3.1 Introduction

Instruments used in this study were all calibrated in less than six months prior to the analysis and were in good working condition. Some of them were tested prior to use to confirm proper functionality. The instruments are categorised by the purpose they served for this study like; synthesis, analysis and application. Synthesis equipment (laser ablation/carbolite furnace) was used for the synthesis of the nanomaterials. Analysis equipments were used to identify material physical, structural and textural properties (HRTEM, HRSEM, BET, XRD, TPD and DRIFTS). Application begins with details of nanofabrication of nanowire based devices then the instruments that were used to analyse their properties such as gas sensing performance.

3.2 Synthesis of Silicon Nanowires

3.2.1 Laser Ablation Technique

Laser ablation system used for the synthesis of SiNWs consisted of three interconnected subsections such as (i) laser source and optics (ii) carbolite furnace and (iii) mass flow controller as shown in Fig. 3.1. The laser source was a Quanta-Ray PRO-270 Nd:YAG (neodymium doped yttrium aluminium garnet) equipped with a laser beam (green light) with a wavelength of 532 nm. Carbolite furnace was used as the growth chamber where a 25 mm quartz tube holding the pellet was placed. The flow-rate of a gas was controlled by a mass flow controller MKS from Vacutec interfaced with a turbo pump. The laser head and furnace were aligned parallel on an optical board prior to ablation.

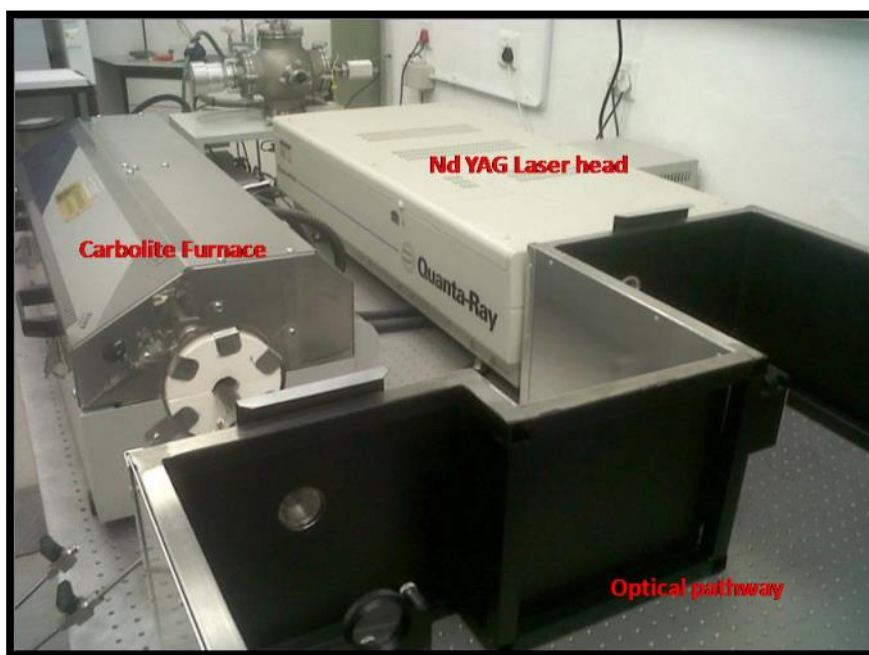


Figure 3.1: Laser ablation set-up.

3.2.2 Chemical Vapour Deposition Technique Set-up

Synthesis of indium phosphide nanowires (InPNWs) and indium arsenide nanowires (InAsNWs) was carried out in the carbolite furnace as shown in Fig. 3.1. The schematic of the carbolite furnace is shown in Fig. 3.2. The reactants (indium and phosphorus in the case of InPNWs [1]) were loaded into a quartz boat (breadth: 15 mm and length: 50 mm) which was loaded into a CVD quartz tube (diameter: 25 mm and Length: 1300 mm). The precursors were separated by 20 cm distance as shown by distance d in Fig. 3.2. The quartz tube was kept under pressure of 500-700 mbar. The carrier gas flow-rate was measured by a flow meter.

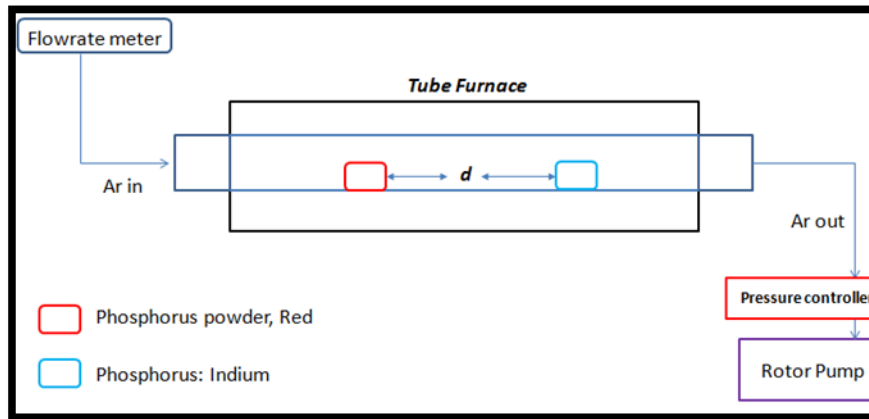


Figure 3.2: Chemical vapour deposition set-up.

3.3 Fabrication of Nanowire based Electronic Devices

3.3.1 Di-electrophoresis (DEP)

Purified InPNWs (1 mg) were dispersed in methanol and ultrasonicated for 20 minutes then centrifuged at 12000 rpm for 20 minutes. The resulting supernatant was decanted and the sediment of nanowires was subjected to the purification process three times to obtain pure nanowires. The patterned substrate (silicone coated with 30 nm of silicon oxide layer) was purchased from nanoelectronic lab at the University of the Witwatersrand, South Africa. The substrate had gold microstructures which were separated by a distance of 2.5 μm as shown in Fig. 3.3.

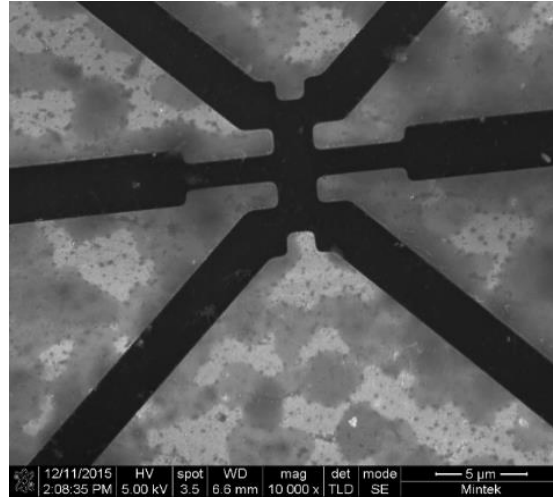


Figure 3.3: Patterned silicon substrate with gold microelectrodes.

The substrate was cleaned by sonicating in acetone, distilled water and methanol for 5 minutes each, drying with dry nitrogen gas after each step. A 20 μl drop of nanowires sediment was drop casted onto the substrate and a voltage of 5V was applied across the electrodes. The potential difference created an electric field causing the nanowires to align on top of the electrodes [2] as shown in the experimental setup in Fig. 3.4. The DEP probes were connected to an alternating current at 5 volts at a frequency of 1 MHz from a function generator. An optical microscope was used to investigate the nanowires alignment after each attempt to make sure that the nanowires contacted both sides of the electrodes.

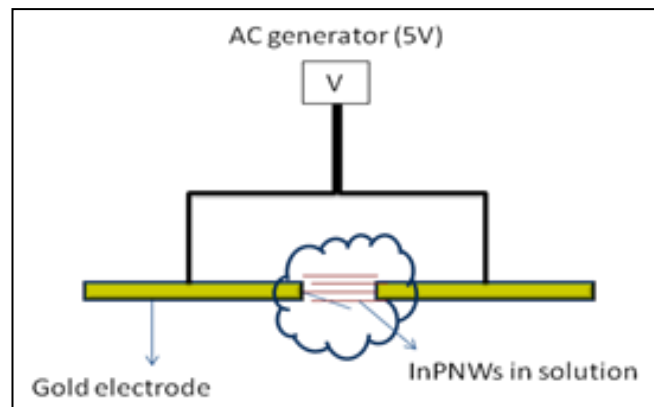


Figure 3.4: Di-electrophoresis experimental setup used to align nanowires across gold electrodes.

3.3.2 Electron Beam Lithography (EBL)

EBL electronic device was fabricated on a silicon wafer coated with a 30 nm layer of silicon oxide. The silicon wafer was coated with 50 μm polymethylmethacrylate (PMMA) resist using a spin coater. The resist was then baked in an oven for an hour at 85 °C. The alignment marks were done using electron beam lithography (EBL) within a high resolution scanning electron microscope (HRSEM). The InPNWs were drop casted on the patterned wafer. The metal electrodes were also fabricated using EBL. The metallisation of gold into the patterns was done using physical vapour deposition (PVD). The lift-off was done using acetone for 48 hours at room temperature [3].

3.4 Characterisation Techniques

3.4.1 High Resolution Transmission Electron Microscope

Digital image of high resolution transmission electron microscope (HRTEM) is shown in Fig. 3.5. HRTEM is a useful technique in determining particle size and morphology of nanomaterials. In TEM an electron beam is propagated through a solid sample in a vacuum and detected on the other side of the sample. These electrons are then detected to produce images which represent the relative extent of penetration of electrons in a specific sample [4]. HRTEM allows for the determination of lattice spacing and their direction. In this work JEOL 2100F, JEM- 200 kV transmission electron microscope operating at 200 kV (Fig 3.5) was used to determine the particle size and morphology of colloidal AuNPs, InPNWs and InAsNWs.

The AuNPs were dispersed in water and nanowires were dispersed in methanol. A droplet of the slurry was placed on a copper grid coated with a formvar-film and carbon. After drying the grid it was then mounted onto the microscope.



Figure 3.5: Image of transmission electron microscope.

3.4.2 High Resolution Scanning Electron Microscopy

Digital image of high resolution scanning electron microscope HRSEM is shown in Fig 3.6. In HRSEM a beam of electrons are propagated to the surface of a solid sample in a vacuum. The electrons are then deflected from the surface of the sample and they are detected by various detectors such as secondary electron detector or back-scattered electron detector [4]. These electrons are then used to formulate a 3-dimensional image of the sample. In this work FEI NOVA nano-SEM 200 HRSEM operating between 5-30kV was used to determine the morphology and textural properties of nanomaterials.

The HRSEM was coupled with energy-dispersive X-ray spectrometer (EDX) analysis to obtain information about the chemical composition of the sample. This is achieved by bombarding a region in the sample with an electron beam which leads to the emission of characteristic X-rays proving information about the concentration of elements in the sample.

The nanowires were dispersed in methanol to make a slurry. A droplet of the slurry was placed on a carbon and fomva -film-coated copper grid. After leaving the grid to dry, it was then mounted onto the microscope.



Figure 3.6: Digital image of scanning electron microscope.

3.4.3 Brunauer-Emmett-Teller

Surface area and pore volume of the nanomaterials were measured by the physical adsorption of a monolayer of nitrogen gas at -70°C from BET adsorption isotherm measurements using TRISTAR 3000 analyser. Nitrogen gas adsorption was used to measure the surface area of the samples. This method is based on capillary condensation, and the equivalent capillary model is used, in which different pores are treated as capillaries with different sizes and the porous body is the combined body of these capillaries. The pore size distribution can be calculated by the adsorbed quantity of the gas molecules at a specified pressure and temperature. According to the principle of adsorption and capillary, the gas is adsorbed on the pore walls at a certain temperature and the thickness of the adsorbed gas layer increases with the rising gas pressure. Adsorption and desorption of nitrogen were repeated 3 times to obtain an average. The surface area and pore volume of InAsNWs and InPNWs are given and discussed in the later chapters.

3.4.4 X-ray Diffractometer

Fig. 3.7 shows a digital image of X-ray diffraction instrument used for the structural analysis of the samples. The X-ray diffraction patterns used was a D8 Advance diffractometer equipped with Lynx-eye XE detector operated between 5 and 80 2θ angles. It was used to determine nanomaterials (InP, InAs, silicon and AuNPs) crystal structures. This instrument utilizes cobalt X-ray source radiation. The diffraction patterns were collected with an X-ray gun operated at 40 kV and 20 mA. Samples were run in a powders form and were mounted on an amorphous silicon sample holder. Compound identification was accomplished by comparison of measured spectra with the spectra of pure samples from the database (JCPDS, Card No. 4-784).

In the XRD instrument a beam of X-rays with a wavelength ranging from 0.5 to 2 Å, incident to a specimen is diffracted by the crystalline phases of a specimen according to Bragg's law [5] shown in Equation 3.1:

$$\lambda = 2d \sin \theta \dots \dots \dots \text{Equation 3.1}$$

Where d is the spacing between atomic planes in the crystalline phase and λ is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ and the specimen orientation.



Figure 3.7: X-ray diffractometer.

3.4.5 Temperature Programmed Desorption (TPD) equipped with Mass Spectrometer

TPD analysis system used was Micromeritics AutoChem II (chemisorption analyser) equipped with Cirrus mass spectrometer as shown in Fig. 3.8. It was used for adsorption of gases on the surface of InPNWs and InAsNWs. All TPD experiments were carried out with helium as carrier gas (flow-rate 50 ml/min) using a quartz U-tube reactor with 6 mm inner diameter). Prior to adsorption, a mass of 100 mg of the samples was heat treated at 350°C. In a typical TPD experiment, adsorbents (e.g. 5 % CO balanced in He) were passed over the catalyst bed at -50°C at a flow rate of 100 sccm for 30 minutes. Then the reactor was cooled down to room temperature for the start of CO-TPD. All samples were heated up to 450°C at a heating rate of 5°C /min.

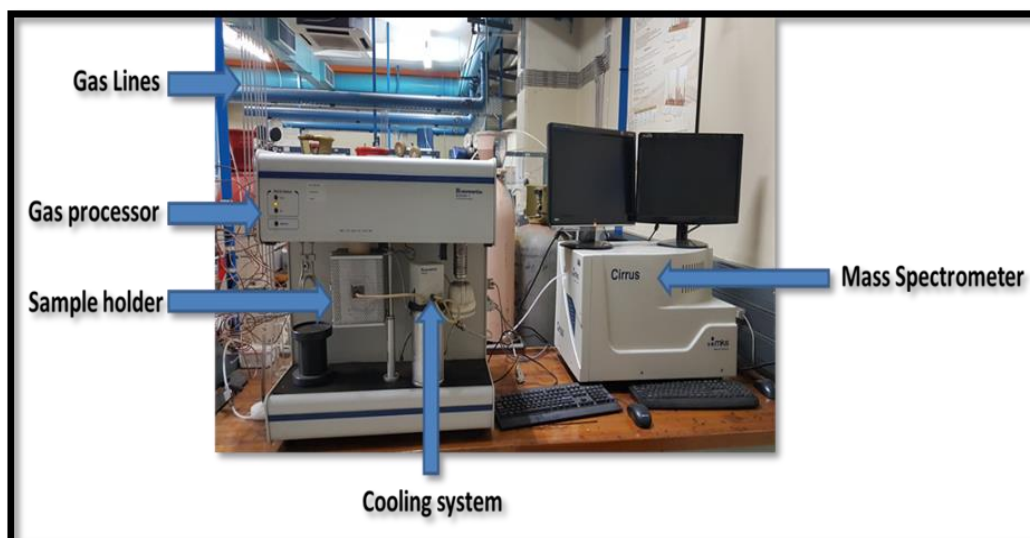


Figure 3.8: Digital image of a temperature programmed deposition system.

3.4.6 Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

The DRIFTS studies were carried out in a DRIFTS cell using Nicolet 5700 FT-IR equipped with InGaAs detector and XT-KBr beam splitter. The DRIFTS cell was equipped with heating elements that could go up to a temperature of 200 °C measured by thermocouples. The DRIFTS cell was connected to a gas-handling unit to measure in-situ DRIFTS spectra in the presence of a gas. A mass of 100 mg of the samples was loaded into a DRIFTS cell equipped with CaF₂ windows. Spectra were collected at a resolution of 4 cm⁻¹ on a Perkin-Elmer 1720 FTIR spectrometer. Gases were led into the cell via a computer-controlled gas blender and exit gases were analysed by a Baltzers Prisma QMS. All samples were heat treated at 120°C in helium 20 sccm for 30 minutes prior to DRIFTS studies.

3.5 Gas Sensing Instrument

KENOSISTEC KSGAS6S gas sensor test system (Fig. 3.9) was used for gas sensing analysis of the samples. The system consisted of a sample stage, an air mixer and a dry air inlet carrying dry air into the mixer, four different gas inlets, and mass flow controllers to control the amount of gas into the chamber. There were six KEITHLEY Pico ammeters to measure conductance of the sample and six heaters that supplied voltage across the sample.

The active material is added over metal electrodes mounted on to a ceramic substrate (heating elements on the rear side). The electrodes are connected to the metal contacts of the machine. Voltage is applied across the electrodes and electrical current is measured. The heaters are used for gas desorption from the active material.

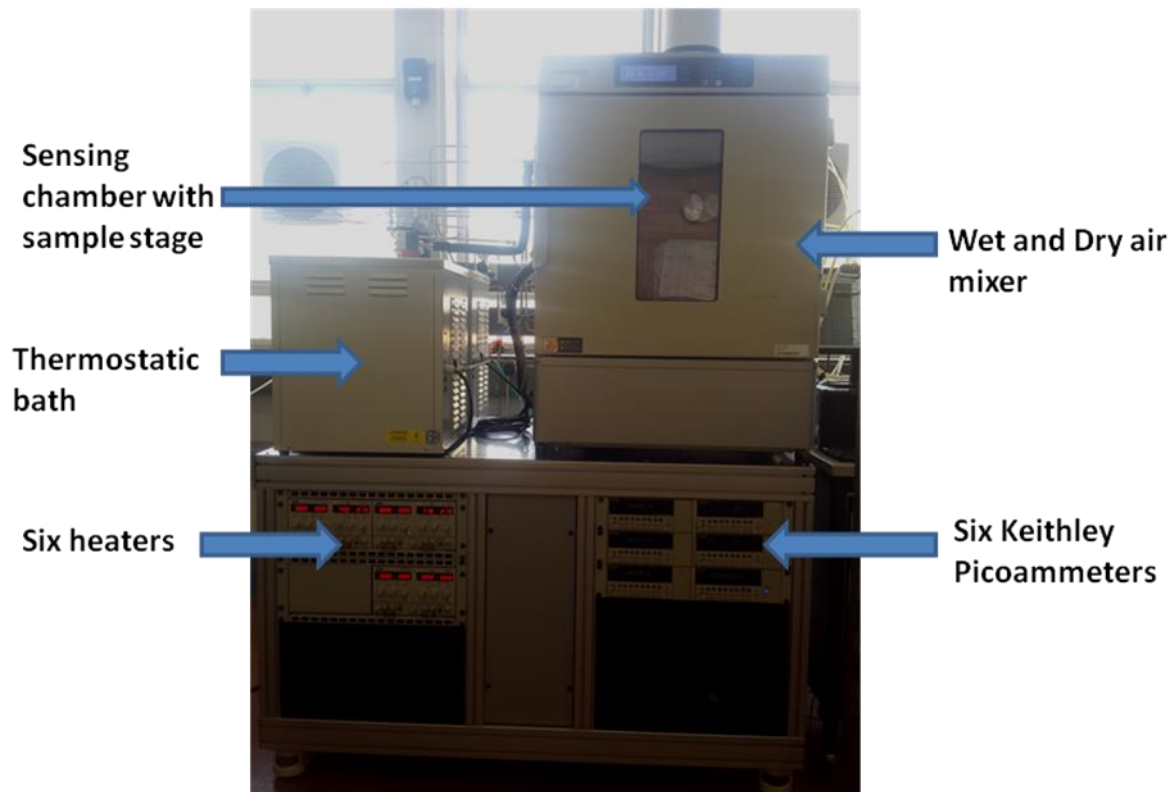


Figure 3.9: Gas sensing system.

3.6 References

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Platonic Gold Nanocrystals: Formation of Icosahedron and Decahedron Nanostructures through Twinning Mechanism

4.1 Introduction

Gold nanostructures are known to be the most stable among the noble-metals [1-3]. The advent of nanotechnology has accelerated interest in controlling anisotropic nanostructures of gold primarily because of their unique optical and electronic properties, controllable size dispersion and morphology, and surface functionalization. Interestingly, there exists a direct correlation of gold nanostructures and their size, shape, crystal phase and surface properties [3].

Currently there are various methods reported for synthesis of gold nanostructures [4-10]. These include seed-mediated, template-directed and defect-mediated growth, among others [7-10]. While progress has been made in synthesizing gold nanoparticles with controlled morphologies and crystal structures much is yet to be done in order to gain new insights in the synthetic method, mechanisms of formation, and material properties. Thus, in order to understand the relationship between the crystal structure and shape [4]. To this effect “Bravais Law” introduced the concept of lattice, which suggests that crystals are formed as a result of periodic stacking of atoms on lattice planes [11]. The crystal structure of a nanoparticle can be best described in terms of imaginary planes where atoms can be packed. These planes are called lattice planes, which spread through the entire crystal structure intersecting the unit cell at specific points called miller indices. These lattice planes result in crystal structure facets. In the case of face-centred cubic the (111) facets are the most densely packed surface with the smallest surface free energy at low temperature [12]. Using mathematical approach, a crystal lattice should have a symmetry axis of order n . If lattice vectors (T) are incorporated, equation 4.1 is obtained:

$$\vec{T} - \vec{T} = m T \dots \dots \dots \text{Equation 4.1}$$

When equation 4.1 is written in a scalar form and m is an integer, equation 4.2 is obtained:

$$2 \cos [2\pi/n] = m \dots \dots \dots \text{Equation 4.2}$$

Equation 4.2 is only valid for $m = 1, 2, 3, 4, 6$ [13]. This means that the assembly of pentagons ($m=5$) will invariably lead to misfit gaps among the boundaries to be filled with defects ($\approx 7.35^\circ$). This is because the dihedral angle of a tetrahedron is 70.53° . This means I_h and D_h shapes are theoretically improbable to form. A. Mayoral and colleagues gave more insight on the mathematical approach calculations [11].

Platonic solids govern the shapes expected in nanoparticles which are cubes, tetrahedral, decahedral and icosahedral. However, experimentally shapes such as D_h and I_h have been synthesized in sub microscopic ranges. It is noteworthy that decahedral can be elongated to form nanorods or nanowires. The formation of these nanostructures (D_h and I_h) with shape anisotropy is known to be kinetically driven.¹⁴⁻¹⁵ Literature suggests that stable D_h and I_h nanostructures can only be formed when the particle size is ≤ 5 nm [16]. The existence of these nanostructures with size larger than 5 nm suggests that they might be polycrystalline, formed through twinning mechanism.

Various mechanisms for the formation of I_d and D_h have been reported in the literature. A.R Tao and colleagues reported that I_d and D_h are metastable structures that evolve to form octahedrons [1]. In this work the mechanism proposed is different to what has been reported in the literature. To the best of our knowledge, this report is the first of its kind on the synthesis of nanostructures formed via twinning mechanism.

4.2 Experimental Procedure

Gold nanostructures were prepared through a heterogeneous nucleation method. The seeds and the growth solution were prepared separately and then mixed to grow the nanostructures. All the steps are described in section 4.2.2, 4.2.3, 4.2.4 respectively.

4.2.1 Chemicals

Cetyltrimethylammonium bromide (CTAB, 99% purity), Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9% purity), L-Ascorbic acid (>99% purity), tri-sodium citrate dehydrate (>99% purity) and sodium borohydride (NaBH_4 , 99% purity) were all used as

purchased from Sigma Aldrich, (RSA) without further purification. Silver nitrate (AgNO_3 , 99% purity) and sodium hydroxide (NaOH , 99% purity) were used as purchased from Fluka (RSA). Ultra-pure water was used to prepare all the solutions.

4.2.2 Preparation of Au Seeds

The citrate stabilized Au seeds were prepared by mixing 20 mM of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 10 mM of trisodium citrate and high purity water in a glass beaker at room temperature. Whilst stirring the mixture with a stirrer bar at 800 rpm, ice-cold 100 mM of NaBH_4 was added and the stirring continued for 5 minutes. The colour of the solution turned purple upon addition of a trisodium citrate. The seeds were stored in a dark place for at least 2 hours before use.

4.2.3 Preparation of Growth Solution

The growth solution was prepared by mixing 25 mM of CTAB, 100 mM of NaOH , 20 mM of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 100 mM of AgNO_3 and 100 mM of L-ascorbic acid in a beaker while stirring with a stirrer bar. The growth solution was used immediately for the growth of nanostructures.

4.2.4 Preparation of Au Nanostructures

The gold nanostructures were grown by adding 0.1 ml of the seed solution to 1 ml of the growth solution. After gentle shaking for 5 seconds the mixture was added to 10 ml of the growth solution. Repeating the same procedure as before the mixture was added to 100 ml of the growth solution. All the synthesis steps were done at room temperature. The final mixture was left in a dark cupboard for at least 24 hours before characterisation. Characterisation was done using UV-Vis absorption spectra (Lambda 35), X-ray diffraction (D8 Advance, Lynx-eye XE detector), and High resolution transmission electron microscope (HRTEM, JEM-2100F - 200 kV).

4.3 Results and Discussion

Gold seeds and nanostructures were found to be agglomeration free as shown on the TEM images in Fig 4.1 (a) and (c), respectively. Particle size histograms of gold seeds and nanostructures showed that they had average particle sizes of 5 nm and 50 nm, respectively as shown in Fig 4.1 (b) and (d). The nanostructures contained 90% icosahedrons and 10% decahedrons with noticeable size difference. The synthesis method produced nanostructures that are stable over a period of time (monitored for 8 weeks). Au nanoparticle seeds revealed a spherical morphology (Fig. 4.1 a) while a mixture of icosahedrons and decahedrons (Fig. 4.1 b) showed multiple-faceted morphology.

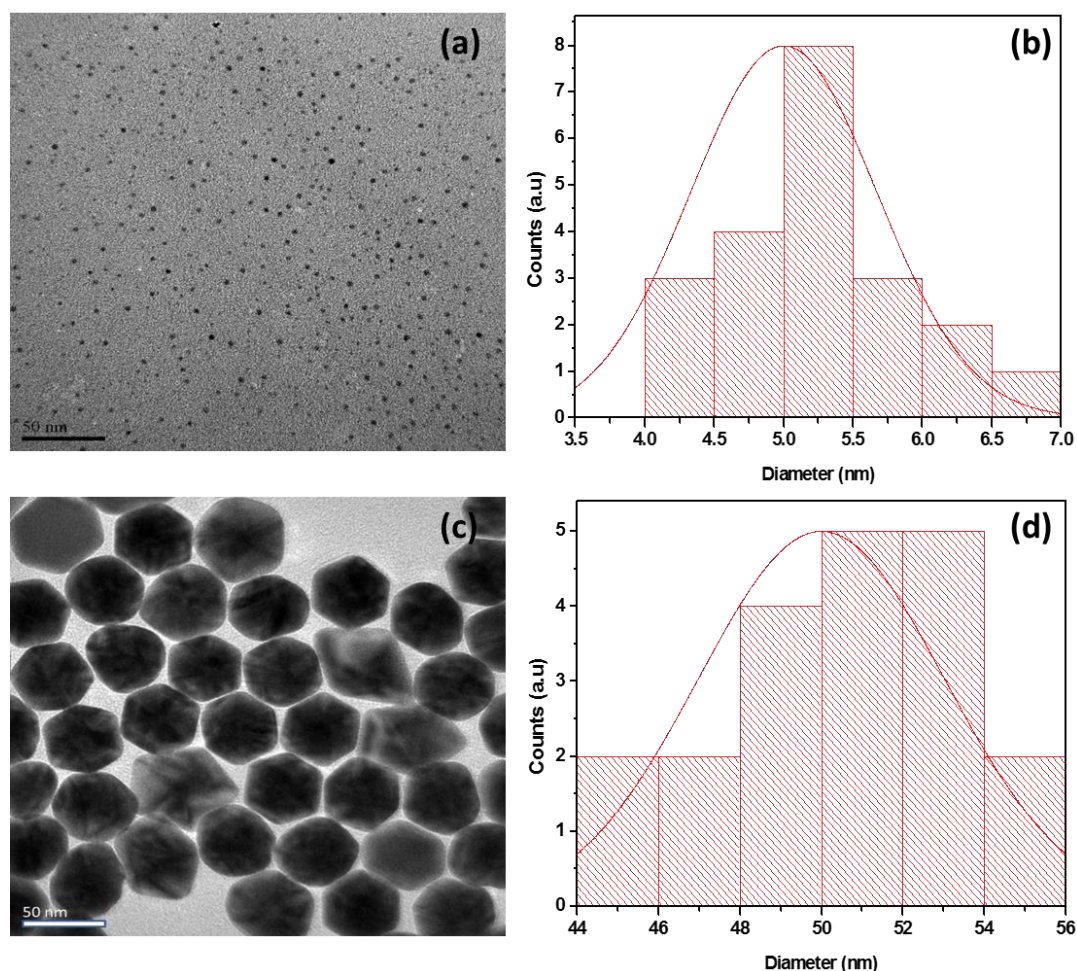


Figure 4.1: TEM images of (a) Au nanoparticle seeds (c) Au nanostructures icosahedrons and decahedrons with corresponding (b) Au nanoparticle seeds and (d) Au nanostructure particle size distribution histogram.

Energy dispersive X-ray (EDX) spectrum confirms that the particles were of elemental gold (Fig. 4.2). The copper (Cu), Iron (Fe) and chromium (Cr) peaks emanated from the sample holder and copper grid in the TEM.

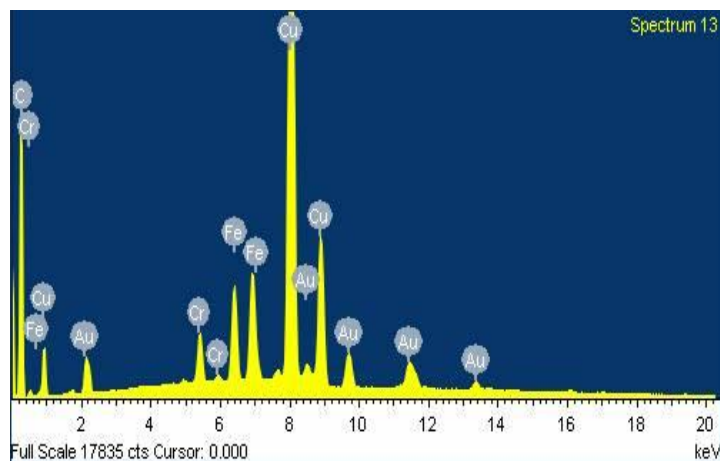


Figure 4.2: EDX spectrum of gold nanostructures.

The UV-Vis spectra of both the seeds and nanostructures show single peak confirming monodispersity as shown in Fig. 4.3 (a) and (b). This confirms that citrate moiety (seeds) and CTAB (growth) have led to well dispersed, agglomeration-free nanostructures. The seeds peak in Fig. 4.3 (a) appears at ≈ 500 nm (absorbance = 0.9) while the nanostructures peak in Fig. 4.3 (b) appears at ≈ 550 nm (absorbance = 1.4). This is a typical Surface Plasmon Resonance (SPR) band resulting from the formation of solid Au nanoparticles in solution. The shift observed in Fig 4.3 (b) is due to size increase of the nanostructures compared to the seeds. This shift is also in line with the TEM observation in Fig. 4.1 (a) and (b) showing that the Au nanostructures were much bigger than those of the seeds.

Ascorbic acid, often used as a mild reducing agent, was used to reduce gold ions. CTAB was used as an atom director to specific faces of the growing crystal. The TEM analysis confirmed that the majority of gold nanostructures were icosahedrons ($\approx 90\%$).

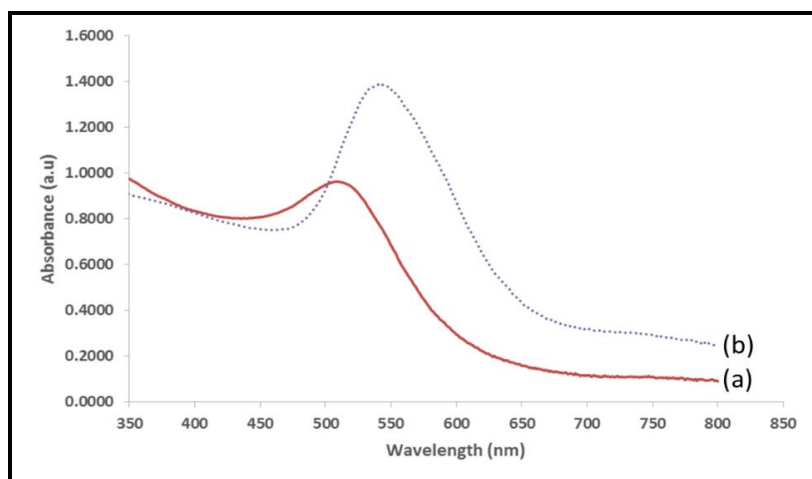


Figure 4.3: UV-Vis spectra showing unimodality (a) Au seeds and (b) Au nanostructures.

X-ray diffraction results for the nanostructures and the seeds show three peaks appearing at 38° , 46° and 55° respectively (Fig. 4.4). These peaks correspond to crystal planes [111], [200] and [110]. The crystal planes [200] and [110] played an insignificant role in growing the nanostructures since CTAB inhibited their growth.

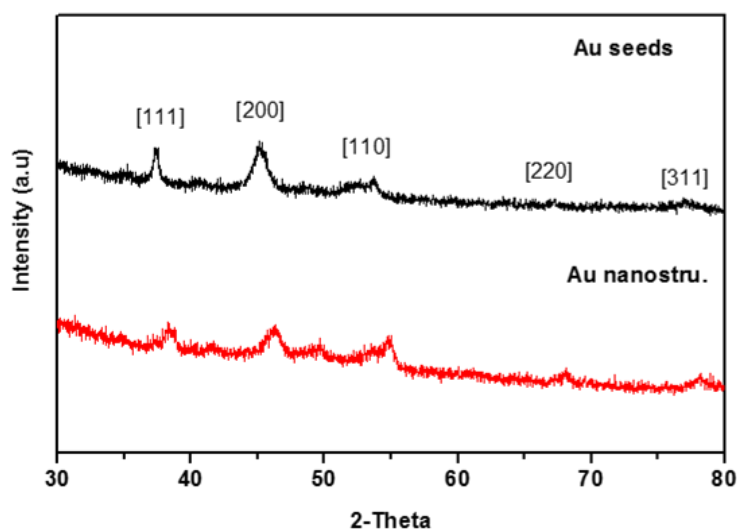


Figure 4.4: X-ray diffraction pattern for Au nanostructures.

As reported elsewhere I_h and D_h particles of gold are thermodynamically unstable above 5 nm [1]. The formation of these particles with sizes well above 200 nm has been observed and reported. However, limited information is available on the mechanism of formation. As such

the formation of this five-fold symmetry has led to an ongoing debate [4, 16]. The formation of these nanostructures with the size bigger than 5 nm is thermodynamically unfavourable unless the growth is kinetically driven [4]. The mechanism that best describes the formation of these five-fold symmetry particles is through twinning of planes [4]. Au has a FCC structure and it is commonplace that growth along the [111] directions in a FCC crystal structure yields tetrahedron configuration which is essential for twinning. During twinning mechanism tetrahedrons are assembled to form a decahedron structure. The presence of CTAB promotes fast growth along the [111] direction in relation to other directions leading to the formation of tetragonal building blocks for nanoparticles [17]. This means that in order for a decahedral shape to form through merging of the tetragons, a resultant misfit gap is generated and subsequently closed through partial disclinations (true for face centred cubic structures). This is because the dihedral angle of a tetrahedron is 70.53° , which implies that the assembly of 5 tetrahedrons to form a decahedron would leave a gap of 7.35° as shown in Fig. 4.5 [4].

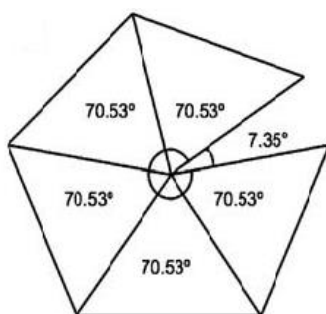


Figure 4.5: Image showing that packing perfect tetrahedral units with 70.53° dihedral angles cannot perfectly form a pentagon (decahedron) without leaving a gap of $\approx 7.35^\circ$ [4]

Partial disclination causes a high strain region in the nanostructure which can be released by heating the nanoparticle [18]. Heating the nanoparticle releases the strain which leads to the plane boundaries moving apart causing plane boundary delamination.

Twinning occurs when atoms or molecules attach to a growing crystal such that the two crystals appear to be growing into or out of each other [4, 19]. According to H. Fuess *et al*, the characteristics of materials that favour twinning are (i) FCC or diamond cubic (ii) low twin boundary energies and (iii) surface energy anisotropy [16]. In the FCC and diamond

cubic materials the stabilizing agent plays an important role in blocking some facets so that certain facets can grow faster than others [20]. The I_h and D_h are equilibrium structures that are kinetically driven and are built by tetragonal subunits. These structures minimize their surface energy by taking a spherical shape which is achieved through the formation of an icosahedron.

Based on the results obtained in this investigation the mechanism of formation of both I_d and D_h is slightly different from what is in the literature. In order to form a decahedron structure the two planes closest to the gap must be closer to each other to close the gap (through partial disclination). Closing the gap causes a particular boundary to be strained. In order to show that all of these steps are necessary for the formation of decahedrons it is important to look closely at the plane boundaries of the particles. Decahedron (Fig. 4.6 a) and icosahedron (Fig. 4.6 b) particles show fringes in different orientations. This phenomenon is suggestive of the presence of polycrystallinity of particles with 5 crystallites arranged to form each particle. This further suggests that these particles are formed through twinning mechanism which is consistent with the literature [4]. CTAB is well known for promoting fast growth along the $[111]$ direction in gold crystals as it weakly binds to it rather than other planes [16]. Electron diffraction (Fig 4.6 (a) inset) on a single particle showed a complex pattern, indicating that the particle was composed of multiple crystal domains. The selected area electron diffraction (SAED) shows that the plane along which the particle is viewed is a $[111]$ which is consistent with the XRD results (Fig. 4.4).

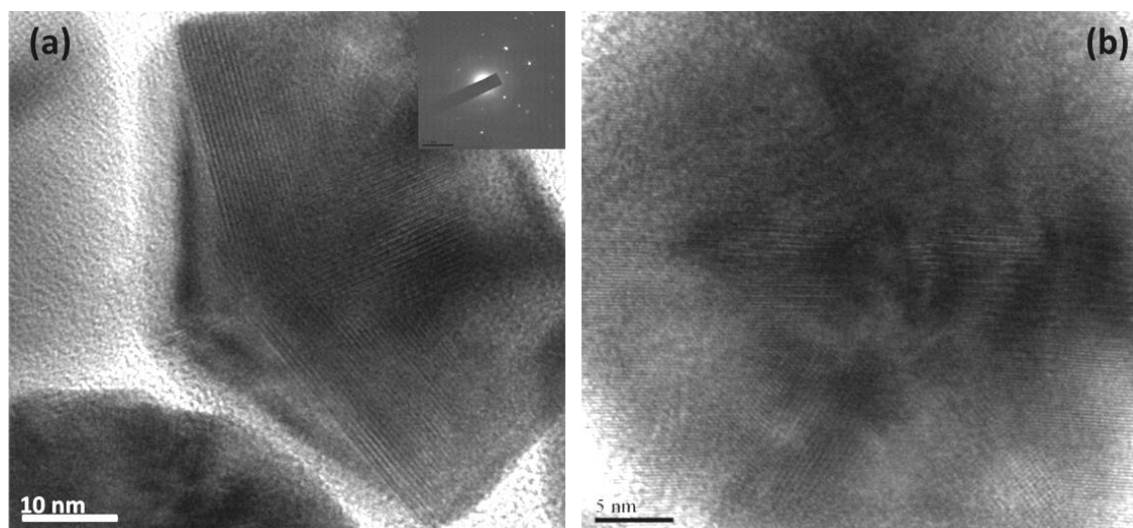


Figure 4.6: HRTEM images (a) decahedron particle, SAED insert showing [111] indexes (b) icosahedrons particle.

In order to show that Au particles were formed as a result of twinning mechanism, they were subjected to electron beam radiation for 10 minutes. It was clear that the exposure for 10 minutes leads to delamination along certain plane boundaries (Fig. 4.7). The strain caused by partial disclination is distributed along the entire particle causing minimised strain in all the plane boundaries. Upon exposure to the electron radiation, any plane boundary can delaminate to relieve the stresses. Figure 4.7 shows that the particle delaminated in two (2) plane boundaries instead of one (1) confirming strain distribution.

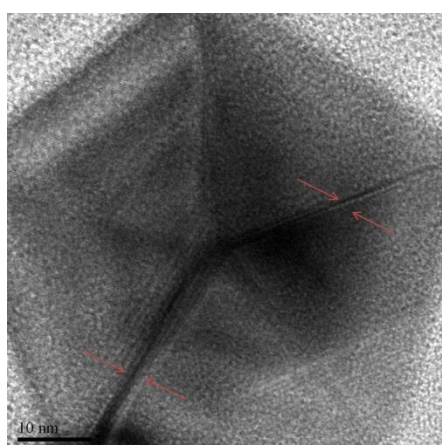


Figure 4.7: HRTEM image showing delamination between the planes.

The delamination that occurred at high temperature upon electron irradiation is irreversible as the sample is cooled down to room temperature. However, it should be noted that the irradiation was done on a sample mounted on a copper grid (TEM) implying that delamination was a solid state phenomenon. The beam was removed from the particle to allow it to cool down to room temperature. The particle delamination was observed after cooling the particle. In-order to evaluate reversibility of the gap, the heating was also done in solution. This sample (colloidal solution) was heated to 300°C for 30 minutes using an oil bath. It was allowed to cool down to room temperature before TEM analysis, this was considered liquid state. The liquid state results were inconclusive in terms of reversibility of the gaps. The results showed no delamination, which could mean two things. The oil bath temperature was either insufficient to cause the delamination or the delamination did occur but was temperature dependent and reversible upon cooling in solution.

Therefore, it was confirmed that the particles grew according to the mechanism shown in Fig. 4.8. The decahedrons are a metastable phase between a tetrahedron and an icosahedron. The formation of icosahedron from a tetrahedron as shown in Fig. 4.8 is ascribed to thermodynamic reasons, which suggest that a sphere is the most stable configuration.

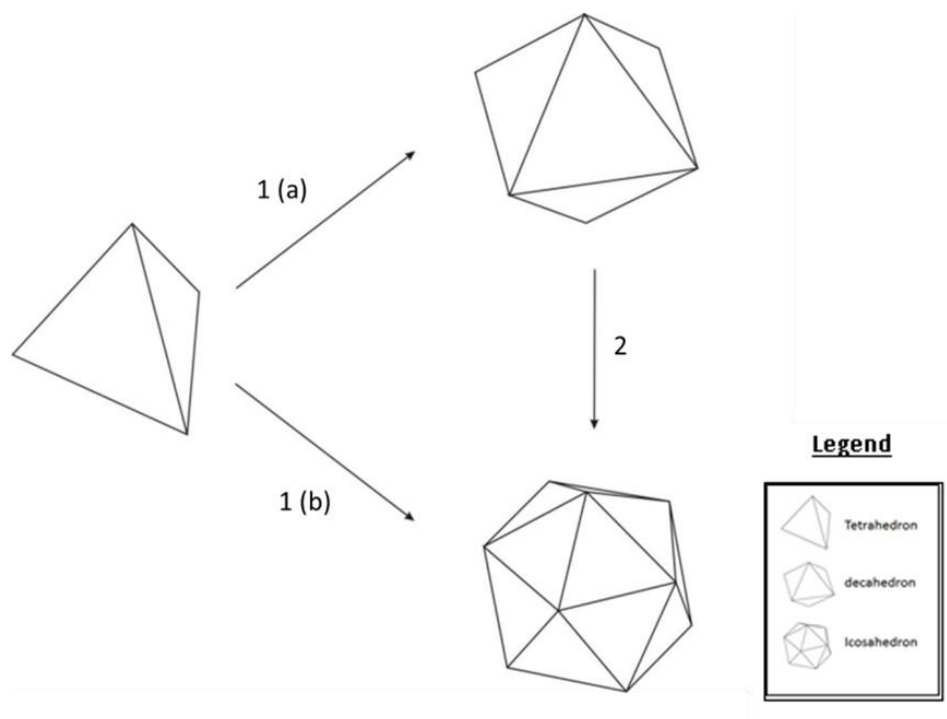


Figure 4.8: A scheme showing the mechanism of formation of I_h and D_h particles.

Therefore, the structure closest to the sphere is more thermodynamically favourable [21, 22]. This is consistent with the observation made by Y. Wang et al, who showed that the more spherical particles exhibited better thermal stability [23]. In the case of formation of decahedron size compatibility and alignment of boundaries are essential for twinning and lead to overall distribution of stress. Size mismatch tends to promote uneven distribution of defects at the boundaries which may lead to the formation of asymmetrical and unstable structure. It must also be noticed that decahedron crystallites cannot grow very large due to limited tolerance to the configurational stress. The fast handling of the seeds during growth favours growth kinetics over thermodynamics. Decahedron being kinetically favoured undergoes a facile nucleation with different formation time whereas the nucleation of icosahedron requires a relatively higher degree of supersaturation. Results show that icosahedron is formed in high yield (90 %) while decahedron resembles intermediate yield (10 %). This clearly suggests that icosahedron is formed via the formation of decahedron and through the assembly of tetragon.

While further crystal growth of decahedron is limited due to configurational stress secondary growth initiated from the boundaries is possible for icosahedron. This occurs through a shell-by-shell growth as edges of icosahedron are twin boundaries. But this will require sufficient supply of gold atoms in order to ensure that the icosahedrons continue to grow. While the mechanism of formation could be explained it must be noted that there are several factors that influence the formation of these platonic structures. These will include method of synthesis of nanostructures, nature and type of stabilizing agent, and size of the nanoparticles.

4.4 Conclusion

Icosahedrons and decahedrons were successfully synthesized through a fast handling of seeds which produced these kinetically favoured nanostructures. The fast handling of the seeds and the small amount of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in the growth solution aided in the formation of kinetically favoured nanostructures, decahedron. These subsequently became the building block for icosahedron. The gold decahedra and icosahedra nanostructures grew through twinning mechanism. The mechanism proceeds through a 2 step process which leads to a more thermodynamically stable configuration.

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Synthesis of Gold Nanoparticles: The Effect of Stabilisers on Morphology**5.1 Introduction**

Gold nanoparticles (AuNPs) occur in various morphological features including spherical, rectangular, triangular, etc. Spherical AuNPs are the most studied because of their unique optical properties and band structure that is dependent on particle morphology [1-6]. AuNPs have relatively superior stability in aqueous media than other metals such as silver [7] making them ideal for application in catalysis [8], electronics [9], optical [10-11], surface enhanced Raman spectroscopy (SERS), etc. [12]. However, very little is known about triangular and hexagonal AuNPs [13]. Optical properties of non-spherical AuNPs have multiple absorption bands [13-17].

There are different synthesis methods reported for the AuNPs like Turkevich method [18], Brust-Schiffrin method, Martin method, Sonolysis [18-21], etc. Amongst these methods, Turkevich is the simplest and most cost-effective [18]. The use of citrate as a reducing agent is important because it produces a more uniform particle size distribution than that produced with borohydride. Furthermore, the use of citrate is known to greatly improve the stability of Au gold colloids. Thus, the stabilizing effect of protective surface layers on the metal particles is commonplace. The stability of citrate-reduced colloids is ascribed to the formation of such a layer during the reduction process. In Turkevich method, sodium citrate is used as both stabilising and reducing agent. The loading ratio of gold to citrate is important for balancing surface charge, which leads to size-selective formation of AuNPs [22-23]. Zukoski et al, reported on the stabilisation of Au colloids showing that citrate ions have preference for gold crystal planes [24-25]. The choice of stabiliser influences the size, size distribution, and shape of the AuNPs. Bulk stabilisers tend to leave active crystal planes on the AuNPs which could lead to agglomeration [25].

Selectively controlling size, size distribution, and shape can be overcome by carefully choosing a model system to understand the key factors that govern the formation of nanoparticles, in the presence of stabilisers and reducing agents [26-27]. This provides

guidelines to explain the synthesis of AuNPs with size- and shape-tuneable properties. The approach is to take advantage of the chemistry of interaction between ligand molecules and the surface of AuNPs [28-29]. The seed-mediated method of synthesis of AuNPs holds promise for the controlled synthesis of small-sized nanoparticles and as such has attracted much attention in recent years [30]. However, although this method provides a much-needed control of size and shape, the mechanism of formation remains enigmatic [31]. It has been reported elsewhere that silver (Ag) ions act as a surface-specific stabiliser in the seed-mediated process [32]. Thus, Ag is selectively deposited on the [110] facet of the Au particle thereby inhibiting growth from this facet and promoting the growth of one-dimensional feature along the [100] direction [33-34].

In this study, the influence of choice of stabilising agent on gold nanoparticle size and selectivity towards nanoparticle shape is reported. Sodium citrate and CTAB are used for the synthesis of AuNPs and are compared for size control and shape selectivity. The interaction of these stabilising agents with the surface of AuNPs as shape-directing agents is discussed. The stabilisers will be used in the preparation of gold seeds and the effect of this on AuNPs is elucidated. Furthermore, investigation of the effects of varying weight percentage of citrate to gold on the size of AuNPs is elucidated.

5.2 Experimental Procedure

5.2.1 Chemicals used

Cetyltrimethylammonium bromide (CTAB, 99% purity), Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, >99.9% purity), L-Ascorbic acid (>99% purity), trisodium citrate dehydrate (>99% purity) and sodium borohydride (NaBH_4 , 99% purity) were all used as purchased from Sigma Aldrich, (RSA) without further purification. Silver nitrate (AgNO_3 , 99% purity) was used as purchased from Fluka (RSA). Deionised water was used to prepare all the solutions.

5.2.2 Characterization of Materials

Characterisation of materials was done using UV-Vis absorption spectra (Lambda 35), X-Ray diffraction (D8 Advance, Lynx-eye XE detector), high resolution transmission electron

microscope (HRTEM, JEOL-2100F-200 kV) and high resolution scanning electron microscope (NOVA nano-SEM, JEOL 7500F, 30kV) and Atomic force microscope (AFM, Nanoscope, contact mode).

5.2.3 Preparation of Colloidal Gold Nanoparticles

In order to demonstrate the contribution of stabiliser molecules to the crystal growth and crystal size, AuNPs were prepared from tetrachloroaurate in the presence of either CTAB or citrate prepared seeds. The preparation of citrate stabilised seeds has been explained elsewhere, Chapter 4, sections: 4.2.2, 4.2.3 and 4.2.4, respectively

5.2.3.1 Gold Seeds Stabilised with CTAB

In a typical procedure, CTAB stabilised seeds were prepared by mixing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.25 mM) and CTAB (75 mM) in a beaker under constant stirring (800rpm) at room temperature. Then ice-cold NaBH_4 (0.6mM) was added to the mixture and the colour changed from colourless to purple. These seeds were stored in a dark cupboard for at least 2 hours before use.

5.2.4 Synthesis of Gold Nanoparticles: Citrate/Gold Salt weight% Concentration Variation

Spherical AuNPs were prepared through an in-situ nucleation method. The loading (wt/wt %) of 0.04 M tri-sodium citrate to 1 mM tetrachloroaurate was varied from 0.7 to 0.2. This was achieved by adding a mass of tri-sodium citrate of 192.10, 96.10 and 19.20 mg in solution to a mass of 75.83 mg of tetrachloroaurate in solution. The mixtures were then allowed to boil for five minutes under constant stirring then cooled to room temperature. The final mixtures were left in a dark cupboard for at least 24 hours before characterisation.

5.3 Results and Discussion

5.3.1 Part A: The Effects of Stabilizing Agent on the Gold Nanoparticles Shape

Fig. 5.1 (a) and (b) showed the TEM images of CTAB and citrate stabilised gold seeds, respectively. TEM images of both CTAB and citrate seeds showed particles that are well dispersed with spherical morphology. The citrate-stabilised seeds show an average particle size of 3 nm with a relatively narrow particle size distribution of 2-5 nm. However, CTAB-stabilised seeds showed nanoparticles with an average size of 5 nm with a relatively wider size distribution of 3-8 nm. The wider particle size distribution for CTAB is attributed to steric hindrance.

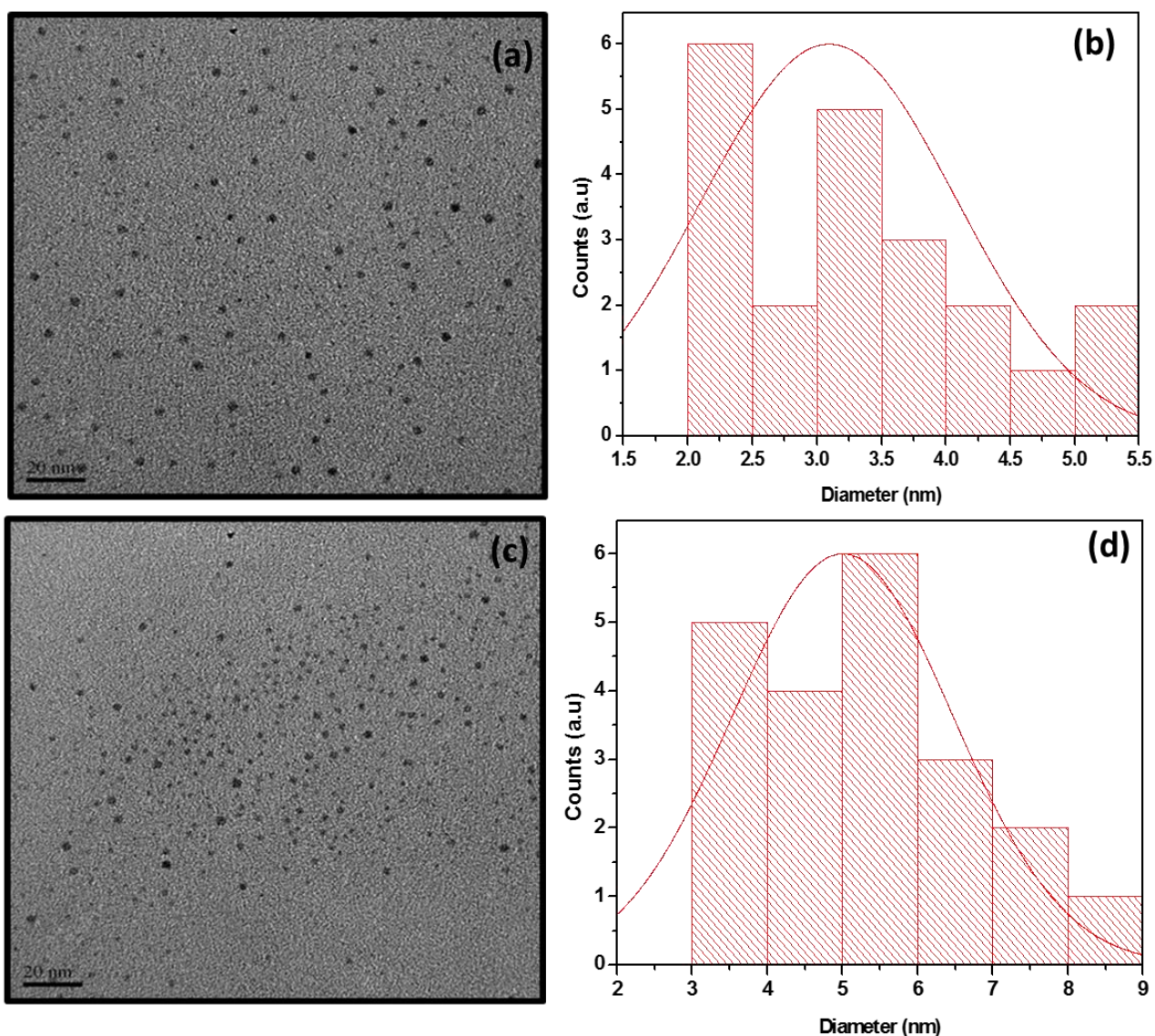


Figure 5.1: TEM images of the gold seeds prepared from (a) citrate and (c) CTAB stabilisers with corresponding particle size distribution histogram for (b) citrate and (d) CTAB stabilised seeds.

Fig. 5.2 showed energy dispersive X-ray (EDX) spectrum of citrate stabilised gold seeds. EDX spectrum of CTAB stabilised gold seeds was found to be identical to that of citrate stabilised seed (not shown). EDX spectrum confirmed the presence of Au while the observed Cu, Fe, Cr and C peaks are ascribed to the TEM sample holder, copper grid, and carbon coating.

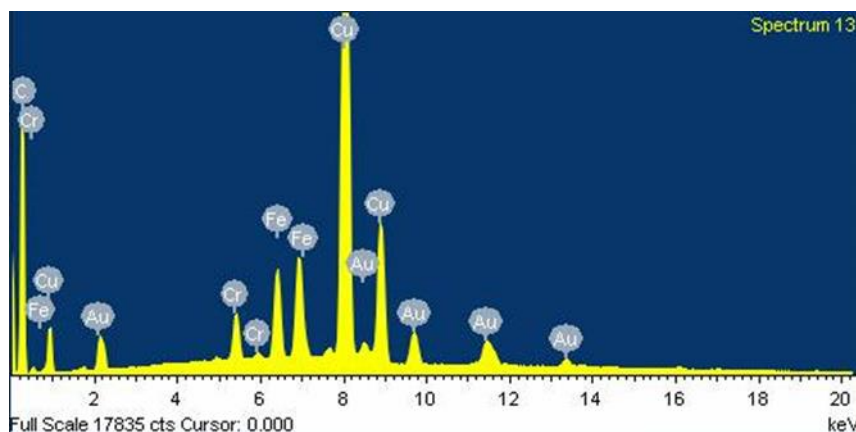


Figure 5.2: Energy dispersive X-ray spectrum of citrate stabilised gold seeds.

UV-Vis results of citrate and CTAB stabilised seeds are shown in Fig. 5.3 (a) and (b) respectively. Citrate gold seeds UV-Vis showed a single peak appearing at a wavelength between 450 and 550 nm which was attributed to a typical Surface Plasmon Resonance (SPR) band resulting from the formation of solid Au nanostructures. The presence of UV-Vis monomodal peak and its position suggests that the nanostructures were elemental gold and monodispersed with similar particle shape [13].

However, the UV-Vis spectrum for the CTAB stabilized Au seeds showed the presence of three distinct peaks at 250-300, 380-450 and 450-500 nm, respectively, and a “shoulder” peak was observed at 300-350 nm. The peaks at 250-300, 300-350, 380-450 and 450-500 were ascribed to the presence of spherical, triangular, hexagonal, rods, respectively [13]. The multimodality of CTAB stabilised seeds UV-Vis spectrum suggests that the seeds are a mixture of multiple shapes of AuNPs. The shapes of the nanoparticles could not be identified from the TEM image of the seeds (Fig. 5.1) due to the small size of the seeds.

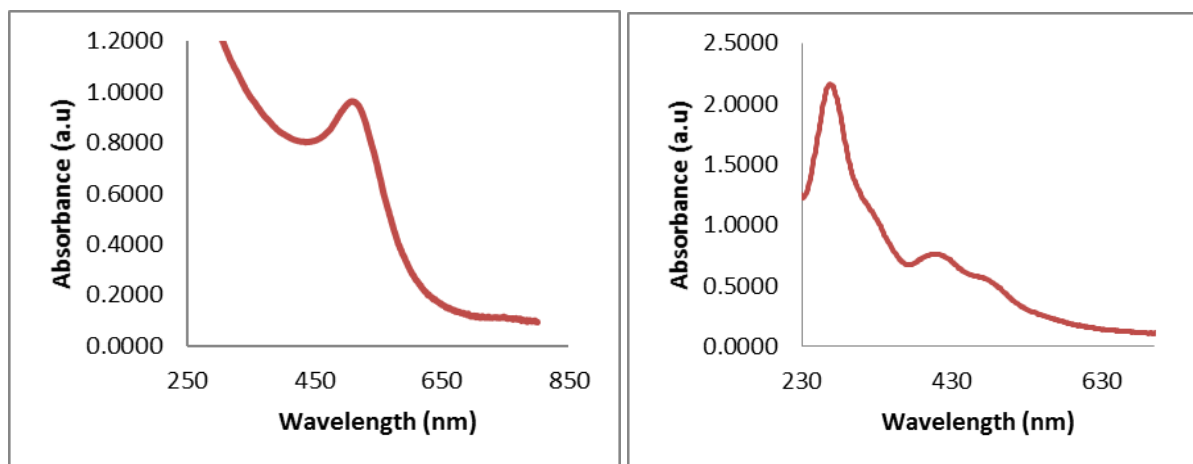


Figure 5.3: UV-Vis spectra of AuNPs seeds prepared from (a) citrate and (b) CTAB stabilisers.

Fig. 5.4 (a) and (b) showed TEM images AuNPs produced from citrate and CTAB stabilised seeds. The use of citrate-stabilized seeds in the synthesis of Au nanostructures has led to the formation of monodispersed nanostructures as shown in Fig. 5.4 (a). In the presence of citrate stabiliser a mixture of the icosahedron (90%) and decahedron (10%) was produced [35]. Both particles (Icosahedra and Decahedra) were measured to be 50 nm in average diameter with a relatively narrow size distribution of 45-55 nm. On the contrary, the use of CTAB-stabilized seeds produced highly agglomerated particles with a wide particle size distribution of 50-200 nm. Furthermore, several anisotropic morphologies were obtained and these included triangles, rods, decahedrons, and spheres. Some of these particles showed irregular shapes as shown in Fig. 5.4 (b).

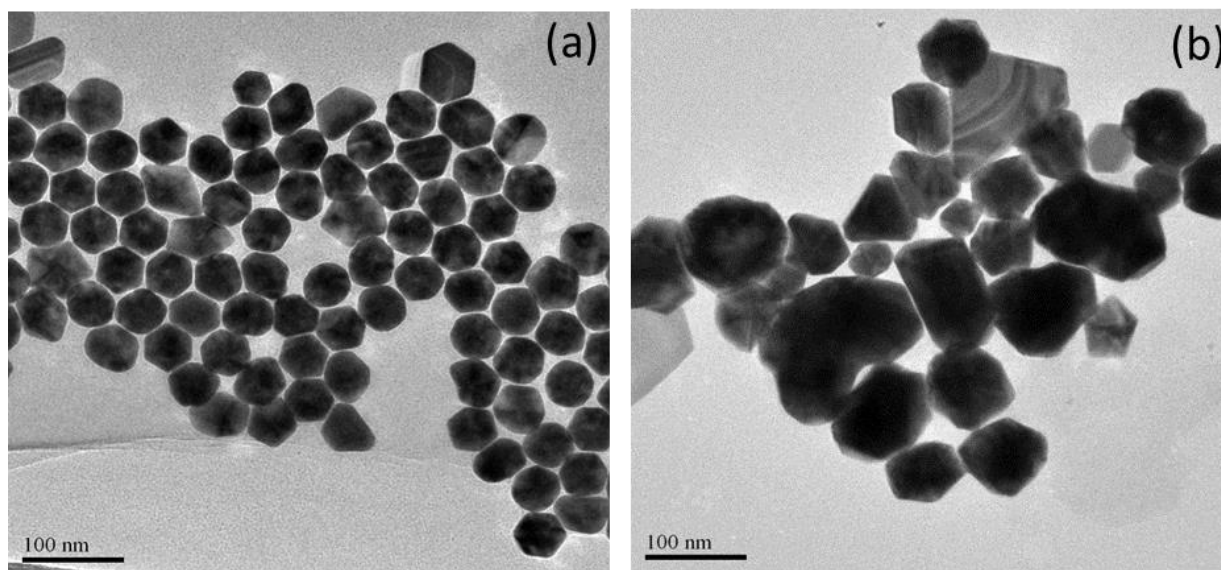


Figure 5.4: TEM images of AuNPs synthesized using (a) citrate and (b) CTAB stabilized seeds.

Fig. 5.5 (a) and (b) shows UV-Vis spectra of AuNPs produced by citrate and CTAB stabilisers, respectively. AuNPs synthesized using citrate stabilised seeds revealed the presence of monomodal peak between 450 and 550 nm and it was found to be similar to that of citrate stabilised seeds. However, higher absorbance was observed along with a red-shift in wavelength for the AuNPs. The increase in absorbance is attributed to an increased concentration while red-shift is attributed to an increase in particle size. AuNPs in Fig. 5.5 (a) showed a well-defined Surface Plasmon Band with maximum absorbance at a wavelength of 528 nm. CTAB stabilised seeds shown in Fig. 5.5 (b) showed a similar increase in absorbance with red-shift in peak position. The absorption spectrum of CTAB-stabilised nanoparticles showed the presence of three bands with maxima at 250-300, 400-450, and 450-500 nm. The presence of these three peaks is indicative of a mixture of anisotropic morphologies. The peak with a maximum at 250-300 is ascribed to the Plasmon band of spherical particles while the remaining two are due to other shapes including tetrahedron/triangular (400-450 nm) and nanorods (450-500 nm).

The TEM and UV-Vis results of AuNPs are consistent with those obtained for seeds. The particles that appear spherical in Fig. 5.1 are actually a mixture of multiple shapes as suggested by UV-Vis of the seeds shown in Fig. 5.2, which could not be identified using

TEM due to their small size. Gold seeds consisting of a mixture of shapes produce AuNPs that are similar in nature.

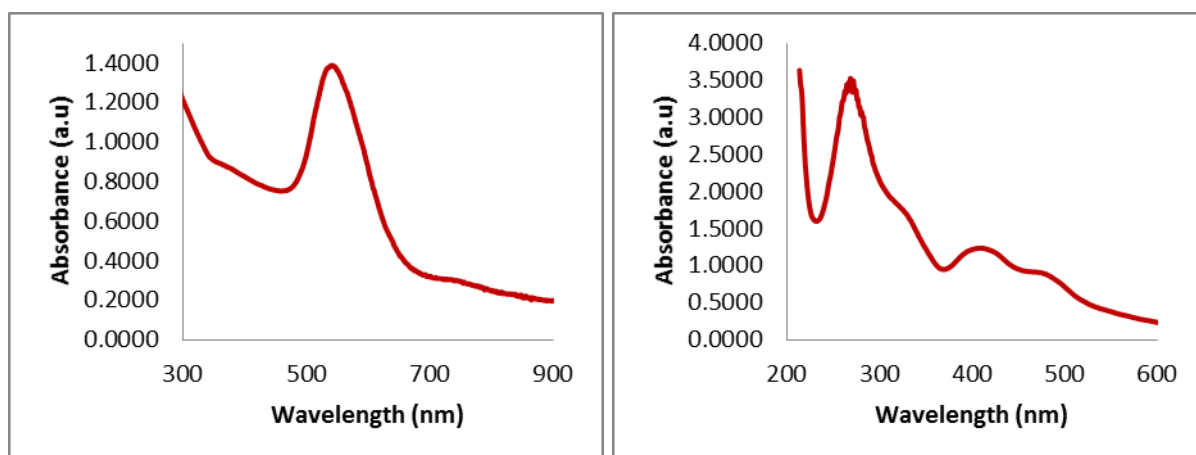


Figure 5.5: UV-Vis spectra of AuNPs prepared using (a) citrate stabilized seeds and (b) CTAB stabilized seeds.

Fig. 5.6 showed XRD patterns of AuNPs prepared using citrate and CTAB stabilised seeds. The XRD patterns of both the citrate and CTAB stabilised gold seeds showed the presence of similar diffraction peaks at 38° [111], 47° [200], 54° [110] and 68° [220] and these are characteristic of crystalline AuNPs. These peaks are typical of face-centred-cubic (FCC) structure of AuNPs (JCPDS, Card No. 4-784). The observed broadening of peaks for both AuNPs is attributed to size effect (small gold crystallite). However, AuNPs prepared from CTAB stabilised gold seeds sample revealed relatively broader peaks than AuNPs prepared from citrate stabilised gold seeds. The broadening was ascribed to inhomogeneous crystal lattice imperfections and grain boundaries in the case of AuNPs (CTAB stabilised gold seeds).

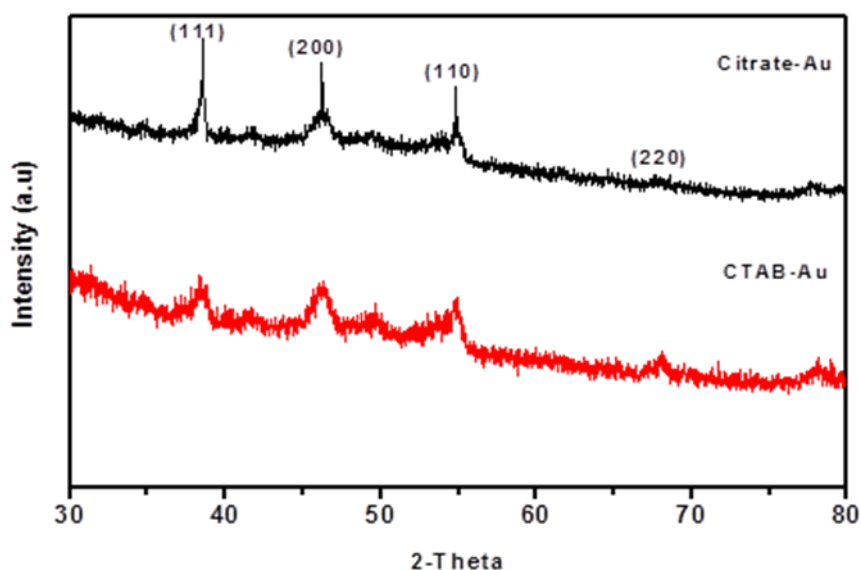


Figure 5.6: XRD pattern of Au nanostructures prepared using citrate and CTAB stabilised seeds.

The optical properties of triangular AuNPs (from CTAB stabilised gold seeds) are known to be tuneable since Plasmon bands are sensitive to the length and sharpness of the tips of the nanostructures. Therefore, the triangular AuNPs were separated from a polydispersed gold mixture using density gradient centrifugation. HRTEM of the isolated triangular nanoparticles is shown in Fig. 5.7 (a). Although, HRTEM showed triangles that look like they are not flat they appear to have a unique triangular shape. However, AFM height mapping and section analysis of the triangles shown in Fig. 5.7 (b) and (c) confirmed that they were not flat triangles, but 3-dimensional tetrahedron instead (to be referred to as tetrahedron from this point on). This is consistent with a unique triangular morphology observed with HRTEM. AFM data could not clearly show whether these particles were tetrahedron or bipyramid. However, literature has shown that the formation of tetrahedron shape is preferential and that tetrahedron structures are a stable precursor to the formation of other structures such as bipyramid, icosahedron, and decahedron [36-37].

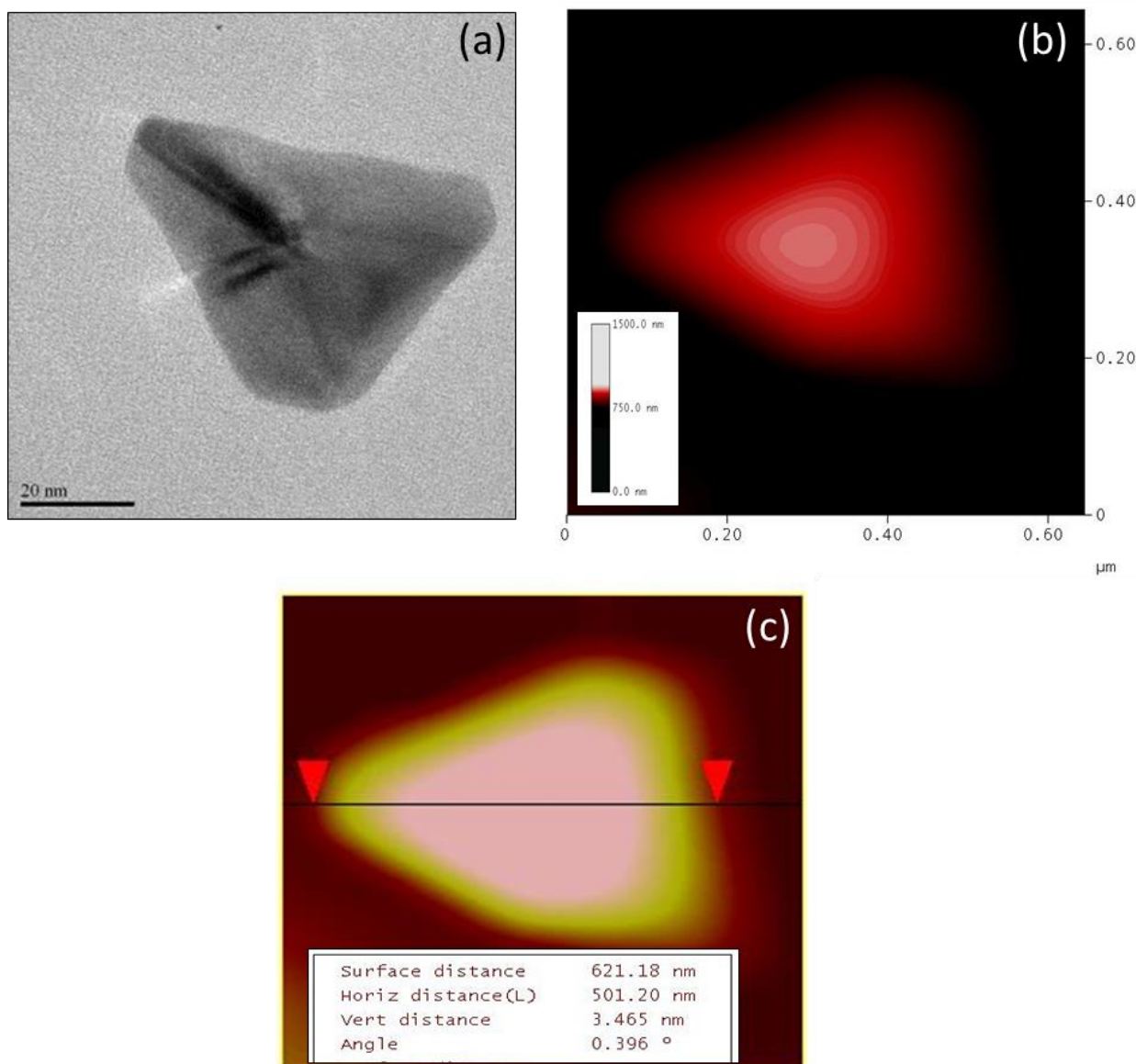


Figure 5.7: Triangular AuNPs analysis results from (a) HRTEM and AFM (b) height mapping and (c) section analysis.

The use of both citrate and CTAB in the preparation of seeds led to the formation of relatively small gold seeds. However, the presence of citrate stabiliser led to a selective formation of spherical nanoparticles. This is probably because citrate is a good shape director favouring a formation of spherical nanostructures. Stabilisation of AuNPs with citrate occurs electrostatically via charge repulsion. The citrate molecule bound to the surface of AuNPs not only controls the formation of spherical particles and size distribution but also prevents particle aggregation.

The growth of AuNPs using CTAB stabilised gold seeds resulted in the formation of AuNPs with different anisotropic morphologies (i.e. nanorods, nanospheres, tetrahedral, etc.). The formation of nanorods along with other shapes is rather unique but can be explained in terms of CTAB binding preferences. The presence of CTAB is fundamentally important because gold as face-centred-cubic metal has no crystallographic driving force for directionality. CTAB molecules might preferentially bind to the long axis face of the growing AuNPs resulting in the formation of nanorods. The polycrystalline seed structure with anisotropic morphology and preferential CTAB binding to the certain facets and/or anisotropic morphology of the seeds played an important role in the formation of nanorods. However, the concentration of the CTAB and the presence of different anisotropic morphology in the seed solution could also favour the growth of other shapes.

It is clear that the type of stabiliser used in the growth of AuNPs influences the kind of chemisorptions or surface capping which in turn has a significant impact on resulting shape of the nanocrystal. Thus, CTAB and citrate could be used for preferential capping and could hinder the growth of particular facets thereby promoting effective control of surface areas of different facets. The results clearly show that the seed structure plays an important role in enhancing epitaxial deposition of the gold atoms and dictates early stage growth direction.

5.3.2 Part B: Effects of Citrate and Gold Salt (wt/wt) on the Size of Gold Nanoparticles.

Fig. 5.8 showed UV-Vis of samples with 0.2, 0.5 and 0.7 % of citrate salt to gold salt. The UV-Vis spectra showed a monomodal peak for all the samples at wavelengths of 520 (0.2%), 517 (0.5%) and 514 nm (0.7%). The presence of UV-Vis monomodal peak suggests monodispersed nanomaterials which show that the presence of citrate moiety led to a monodispersed nanoparticles. The wavelength at which the peaks appear is a typical Surface Plasmon Resonance (SPR) band resulting in the formation of gold particles in solution. The position width and intensity of SPR band are dependent on particle size, shape, concentration, surface-charge, refractive index of the medium and interparticle interactions. The SPR wavelength decreased with an increase in citrate percentage (Blue-shift) suggesting a reduction in the particle size.

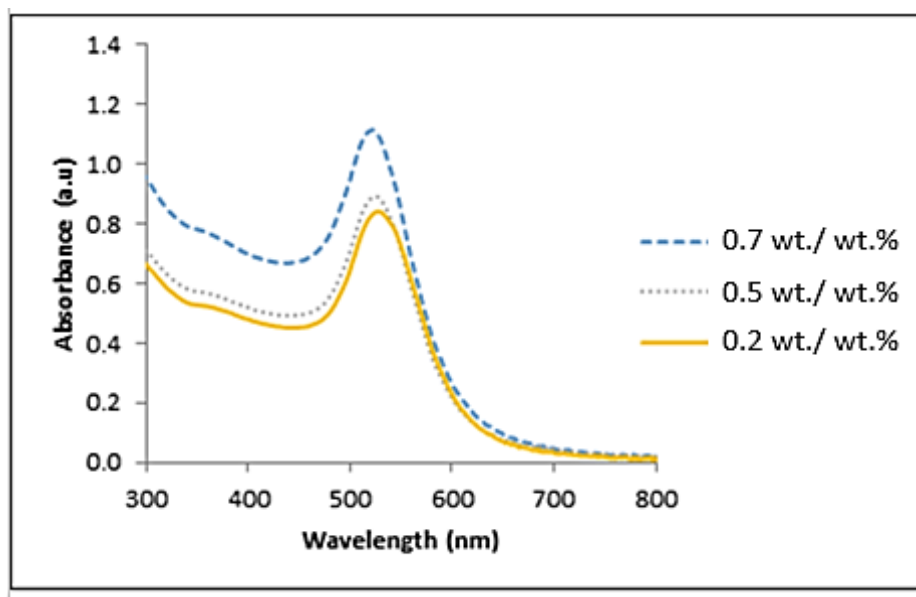


Figure 5.8: UV-Vis spectra of AuNPs with 0.2, 0.5 and 0.7 weight percentages of citrate salt to gold salt.

AuNPs were synthesized by classic citrate (Turkevich et al) method with varying citrate/gold salt ratios. Fig. 5.9 showed TEM images of AuNPs prepared by (a) 0.7 (b) 0.5 and (c) 0.2 % of citrate salt/gold salt ratios with corresponding size distribution histograms with a Gaussian curve fitted into the data, respectively. TEM analysis show that 0.7, 0.5 and 0.2% samples are made up of nanoparticles with average diameters of 14, 29 and 40 nm. AuNP size increased with a reduction of citrate stabiliser weight from 0.7 to 0.2 %. The AuNPs were monodispersed which is in agreement with the single peak observed from the UV-Vis analysis of each sample.

Interestingly, the shape of the AuNPs became increasingly irregular with a decrease in citrate/gold salt ratio. A restrained concentration of citrate molecules resulted in a formation of rod-like and other irregular structures (Fig 5.9).

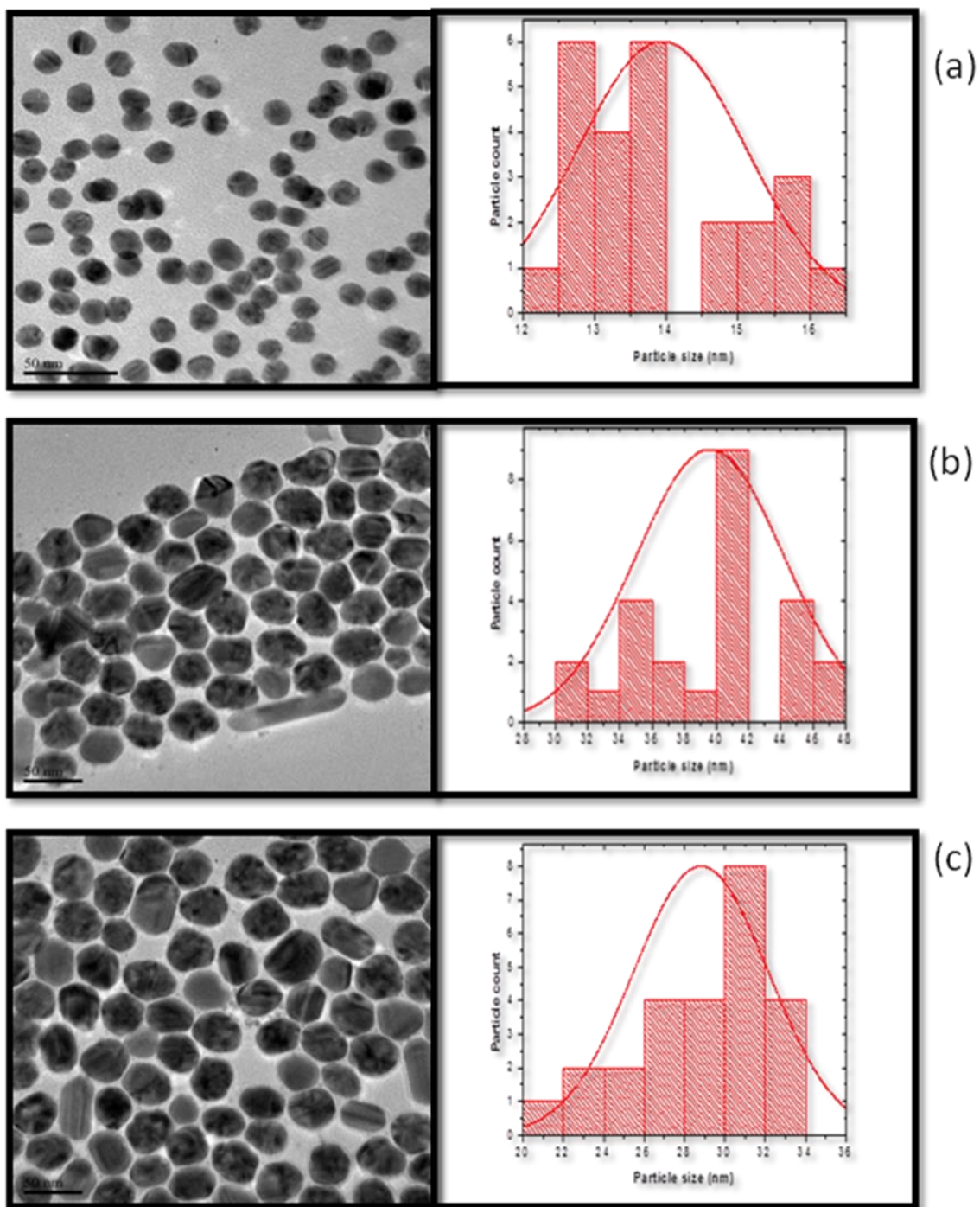


Figure 5.9: TEM images and size distribution histograms of AuNPs prepared with (a) 0.7, (b) 0.5 and (c) 0.2 citrate salt/ gold salt %.

EDX analysis of AuNPs sample with 0.2% (wt/wt) shown in Fig 5.10 confirmed that the particles were those of gold. EDX spectrum of 0.2% sample was similar to those of 0.5 and 0.7 % samples (not shown). The carbon emanated from the carbon coating done in sample

preparation. The EDX confirmation of gold is in agreement with the SPR band position which suggested that the nanoparticles were gold.

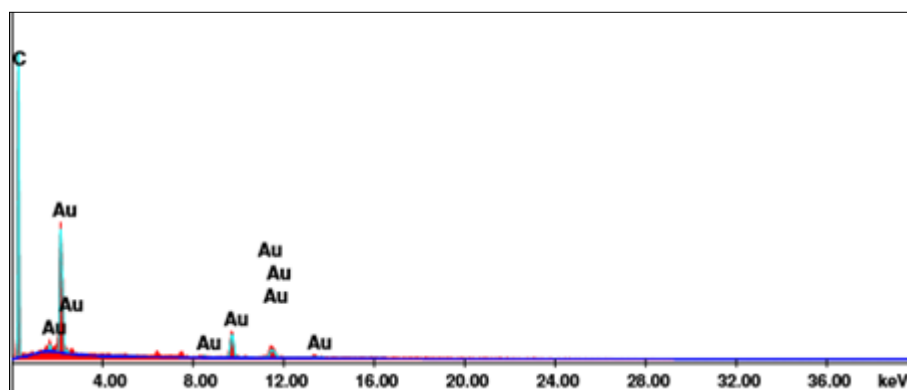


Figure 5.10: EDX results of gold nanoparticles prepared using citrate.

The results clearly show that high concentration of citrate led to the formation of small AuNPs (14 nm). As the citrate concentration was systematically reduced, the size of the nanoparticles increased to 29 nm then to 40 nm. It is noteworthy that the reduction of citrate concentration implies an increase in gold ion concentration. This change in citrate salt/Au salt influences the pH of the reaction mixture thereby affecting the formation of AuNPs. Furthermore, the increase in the concentration of gold salt might have resulted in increased ionic strength emanating from a high concentration of Au salt which could have a direct impact on both the size and size distribution of the AuNPs. However, when the concentration of citrate was reduced to 0.2 %, less stabiliser shielding effect occurred on the AuNPs leading to particle growth. A balance of citrate molecules and Au^{3+} ions is crucial for controlling the size of gold nanocrystals. The citrate molecules get attached to crystallite crystal planes thus hindering growth leading to a formation of specific particle size.

5.3.3 Comparison of the Effects of Stabilizing Agent and Citrate Salt Loading on Gold Salt on the Size of Gold Nanoparticles.

This study revealed that the choice of seed stabiliser is important in order to produce a specific shape of AuNPs. The use of CTAB stabiliser led to the formation of AuNPs with various shapes and sizes. CTAB is a large molecule and could give rise to steric hindrance thereby reducing the number of CTAB molecules on the surface of the gold crystallite. This

could lead to an increase in particle-to-particle attraction resulting in lower surface energy. Particle attraction leads to uncontrollable agglomeration forming larger particles with various shapes. Citrate tends to promote monodispersed spherical AuNPs with narrow size distribution [36]. The stabiliser used for the growth of seeds had an effect on the morphology of AuNPs. A mixture of various shapes of seeds leads to a mixture of AuNPs produced.

Citrate concentration is important in determining the size of the AuNPs. Higher citrate concentration leads to the formation of smaller AuNPs. However, the size increases when the citrate stabiliser concentration is reduced. Variation of the ratio of citrate to gold salt leads to a specific size of AuNPs. The citrate/gold salt range of 0.2 to 0.7% produced AuNPs with sizes between of 14 and 40 nm.

5.4 Conclusion

Citrate and CTAB were compared, under similar conditions, for their strength to dictate the shape of nanocrystals as a thermodynamic tool for controlling shape. The choice of stabiliser renders some facets thermodynamically more favourable by reducing interfacial free energies through chemisorption. Various morphologies of Au nanostructures were successfully synthesized and they depended on the stabiliser choice. The citrate yielded monodispersed seeds and Au nanoparticles with uniform size and narrow size distribution. The CTAB stabilized seeds produced polydispersed nanoparticles which resulted in a mixture of various anisotropic morphologies. When compared with CTAB as stabiliser, citrate is a more selective capping agent for gold nanoparticle in relation to morphology and size distribution. Au/citrate ratio was varied to synthesise different Au nanoparticles sizes leading to different AuNPs sizes (14, 29 and 40 nm). The particles size increase was achieved by systematically reducing the citrate concentration. The optimisation of citrate salt/ gold salt ratio is essential for controlling size, size distribution.

5.5 References

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Synthesis of branched Silicon Nanowires using Laser Ablation

6.1 Introduction

Silicon nanowires (SiNWs) are quasi one-dimensional structure with diameters less than 100 nm. SiNWs have a relatively high surface area to volume ratio owing it to their small diameter and morphology. Unbranched SiNWs have a potential for solar energy harvesting through absorption of incident light. However, these nanowires have relatively low light absorption efficiency. Non-silicon materials such as gallium arsenide absorb light more efficiently than silicon, but these are typically expensive. In order to counteract the performance and cost trade-off, new synthesis methods are required to produce SiNWs with enhanced light absorption efficiency. Branched SiNWs have been reported to have a better potential to improve solar energy conversion in a photovoltaic application through the scattering of unabsorbed light [1].

Silicon is one of the most studied semiconductor materials in both basic and applied research due to excellent properties such as high crystallinity, high surface to volume ratio, improved quantum confinement effects and slow electron-hole recombination [2-8]. Fabrication of electronic device based on silicon has become a blueprint for other nanowire-based electronic devices [9-12]. SiNWs are currently used in energy storage devices, photodetectors, sensors, transistors, etc. [13-14].

There are various methods that have been reported for the synthesis of high-quality SiNWs and these include (i) lithography, (ii) chemical vapour deposition, (iii) laser ablation, (iii) solution phase synthesis, (iv) chemical etching, and (v) epitaxy [9-12, 15]. Most of these methods involve vapour-liquid-solid or vapour-solid-solid (VLS or VSS) growth mechanisms which require a metal catalyst as an initialization agent [16-17]. AuNPs are the most preferred catalyst because of their stability [18]. Metals such as platinum, nickel, copper, and zinc have been reported to show catalytic activity for the growth of SiNWs [19].

The objective of this work is to use Ni and Au as catalysts for the synthesis of branched SiNWs using laser ablation. This is done by (i) incorporating metal catalyst into the silicon pellet and (ii) placing a metal catalyst on a substrate which is separated from the silicon pellet.

6.2 Experimental Procedure

SiNWs were synthesized using laser ablation method. The laser delivered a total energy of 465 mJ to the silicon pellet. The laser head was properly aligned with the furnace on an optical board in such a way that the laser reached a pellet inside the furnace at full power. The furnace housed a 25 mm quartz tube containing a silicon pellet and was set at 1000 °C before ablation. Furnace was connected to a gas system, and a Vacutek MKS mass flow controller interfaced with a turbo pump was used to control the gas flow-rates and pressure, respectively.

6.2.1 Silicon Pellet Preparation

Silicon pellet (diameter: 20 mm) was prepared by pressing silicon powder (Sigma Aldrich, max particle size 45 μm , 99.998% purity) using a hydraulic press at 10k tons for 20 minutes. Three types of silicon pellets were prepared and these included (i) pure silicon pellet (ii) silicon pellet with 1% (wt/wt) of Ni powder (ii) silicon pellet with 1% (wt/wt) of AuNPs. Pure silicon pellet was ablated while a silicon wafer decorated with 20 nm AuNPs was positioned 20 cm downstream of the furnace tube.

6.2.2 Laser Ablation of the Pellet

Each silicon pellet was ablated, separately. The pellet was placed inside a quartz tube with the length of 1.2 m and diameter of 25 mm and the furnace temperature was raised to 1000 °C. The ablation comprised of laser oscillations of 10 s^{-1} and amplitude of 10 μm which delivered laser energy of 465 mJ. The laser was focused on the surface of the pellet for 30 minutes to vaporize the pellet, producing an atomic plume which subsequently condensed to form nanowires. Characterisation was done using TEM, SEM, and XRD.

6.3 Results and Discussion

6.3.1 Synthesis of Gold Catalysed Silicon Nanowires

6.3.1.1 Ablation Pellet Prepared by Incorporating Gold Nanoparticles

The morphology of AuNPs was studied by the use of TEM and the image is shown in Fig. 6.1 (a). Analysis revealed that AuNPs were in spherical form with an average diameter of 20 nm and narrow size distribution of 17–24 nm (Fig 6.1 b). The observed uniform nanoparticles from TEM are indicative of monodispersity nature of the particles. A narrow size distribution of AuNPs suggests a very high surface area and enhanced catalytic activity.

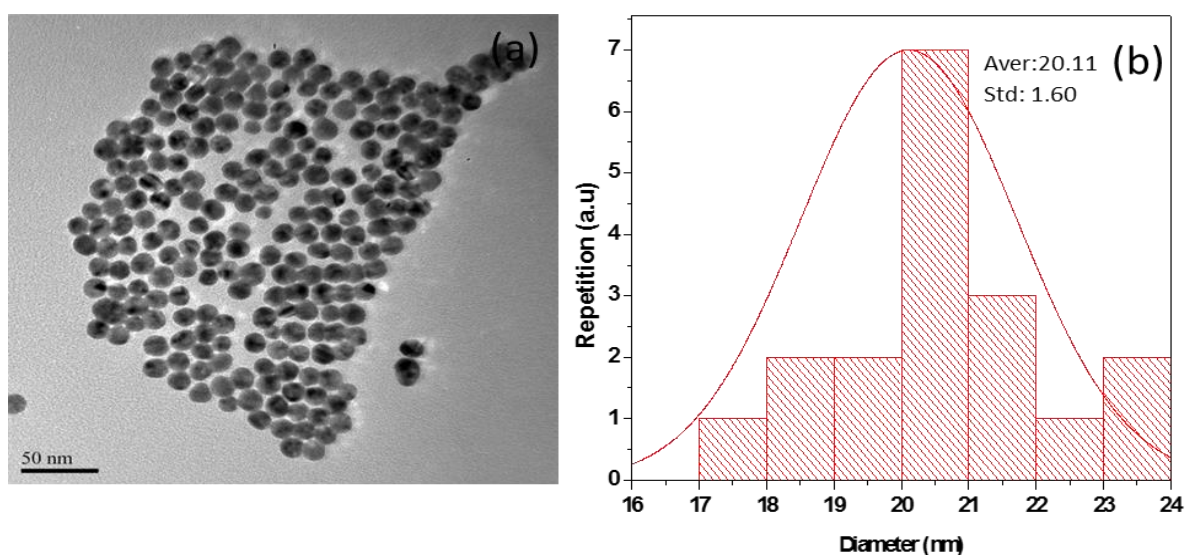


Figure 6.1: (a) TEM image of spherical gold nanoparticles and corresponding (b) particle size distribution histogram with a Gaussian curve fitted to the data.

SEM image in Fig. 6.2 (a) showed SiNWs that are unevenly curved and branched with a uniform diameter. Fig. 6.2 (c) showed SiNWs particle size (diameter) distribution histogram with a Gaussian curve fitted into the data, which showed an average diameter of 20 nm and narrow size distribution of 20–24 nm. The SiNWs diameter and size distribution were homogenous with those of the Au catalyst shown in Fig. 6.1. Curved SiNWs hold promise for flexible and stretchable electronic devices. TEM image in Fig. 6.2 (b) showed SiNWs with a darker tip than the nanowire body, a phenomenon characteristic of a catalyst driven nanowire

growth such as VLS. The dark spherical particle at the tip of the SiNW was confirmed to be gold particle using EDX analysis as shown in Fig 6.2 (d).

The formation of unevenly curved SiNWs with uniform diameter can be explained in terms of synthetic approach, i.e. laser ablation. The furnace temperature was set at 1000°C before ablation. Laser energy of 465 mJ raised the furnace temperature to an estimated value of 1900 °C at the ablation spot [20]. Au catalysts melted at 1064°C and absorbed silicon atoms to a point of supersaturation thus forming a crystalline material. When the temperature decreased to Au/Si eutectic temperature of 363°C, Au catalyst precipitated the silicon atoms forming nanowires [20]. Molten AuNPs have high kinetic energy at high temperature making them move in random directions resulting in the formation of curved SiNWs. SiNWs diameter was found to be dependent on the catalyst diameter as per VLS mechanism [21].

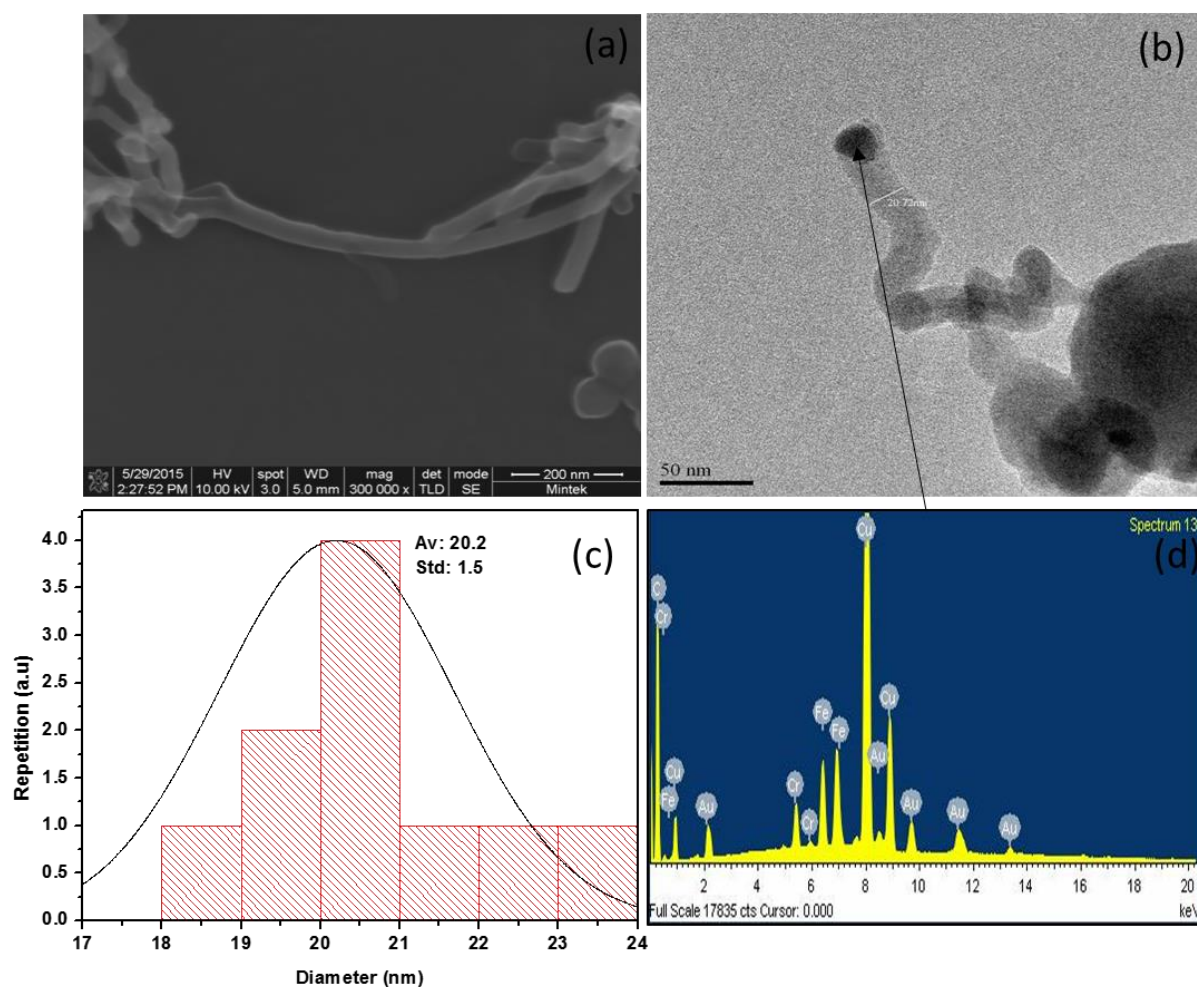


Figure 6.2: (a) SEM and (b) TEM images of silicon nanowires synthesized by laser ablation with corresponding (c) particle size distribution histogram fitted with Gaussian curve and (d) EDX spectrum of silicone nanowires tip.

XRD pattern of SiNWs is shown in Fig 6.3 and it revealed the presence of sharp and narrow peaks suggesting a very crystalline material. The peaks at 2-theta values of 33° [111], 56° [220] and 67° [331] were all indexed to pure silicon. This suggests the SiNWs produced were phase pure.

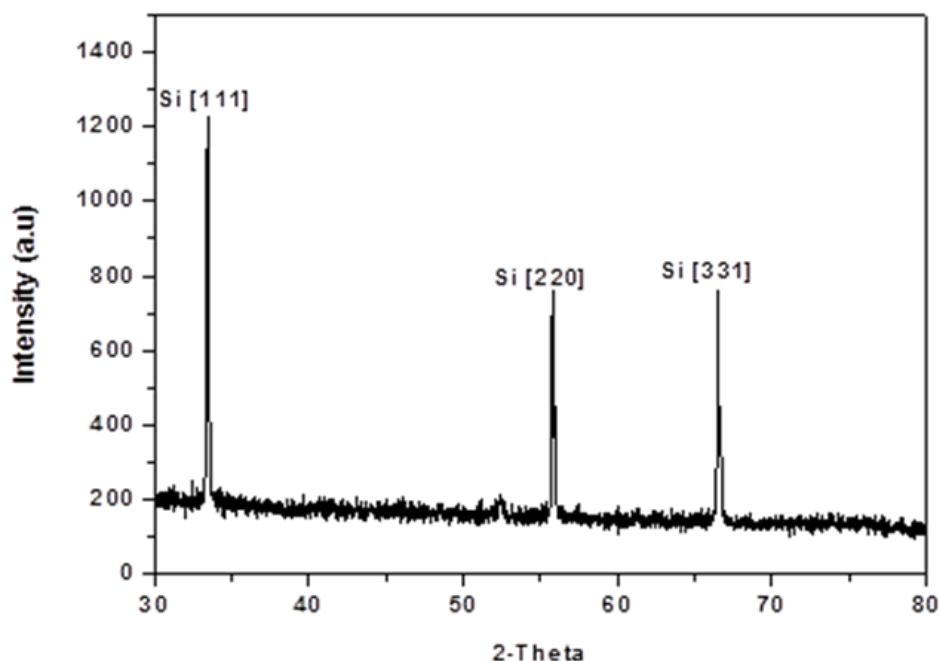


Figure 6.3: XRD pattern of gold-catalysed SiNWs prepared through laser ablation.

6.3.1.2 Gold Nanoparticles drop-casted on the Silicon Wafer

Fig 6.4 showed a SEM image of the AuNPs adsorbed onto silicon wafer by a drop-casting method. The size and size distribution of AuNPs were measured using TEM data as explained in section 6.3.1.1 and shown in Fig 6.1. The arrangement of AuNPs on the surface of the silicon wafer were deposited as individually and as clusters with particle sizes comparable to that of the pristine AuNPs (not deposited on a substrate). The SEM image also revealed an increase in AuNPs density and this is attributed to certain regions of the silicon surface promoting the adsorption of several numbers of particles forming clusters.

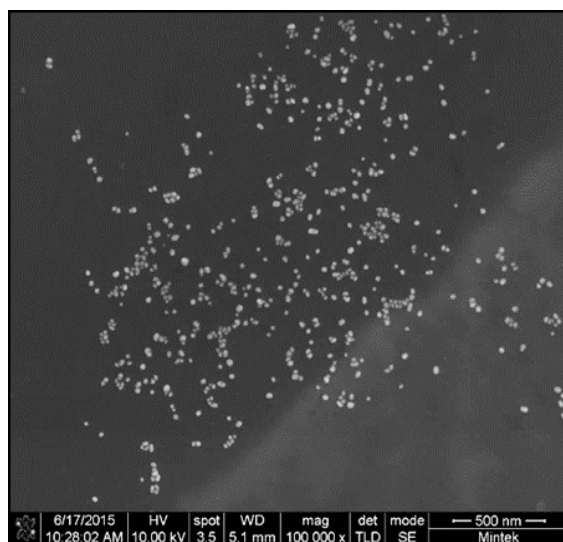


Figure 6.4: SEM image of gold nanoparticles prepared on a silicon wafer.

Fig. 6.5 (a) and (b) showed SEM images of SiNWs grown on a silicon wafer in the presence of AuNPs as a catalyst. SiNWs produced were unbranched and straight with Au catalyst at the tip. Fig 6.5 (c) showed SiNWs particle size distribution histogram with a Gaussian curve fitted into the data showing an average diameter of 2 μm and size distribution of 2.1 μm to 2.3 μm . The diameter size of the SiNWs was inhomogeneous with that of AuNPs used as a catalyst. SiNWs diameter and the AuNP at the tip were significantly bigger than that of pristine AuNPs. This suggests that high synthesis temperature altered the size and stability of AuNPs.

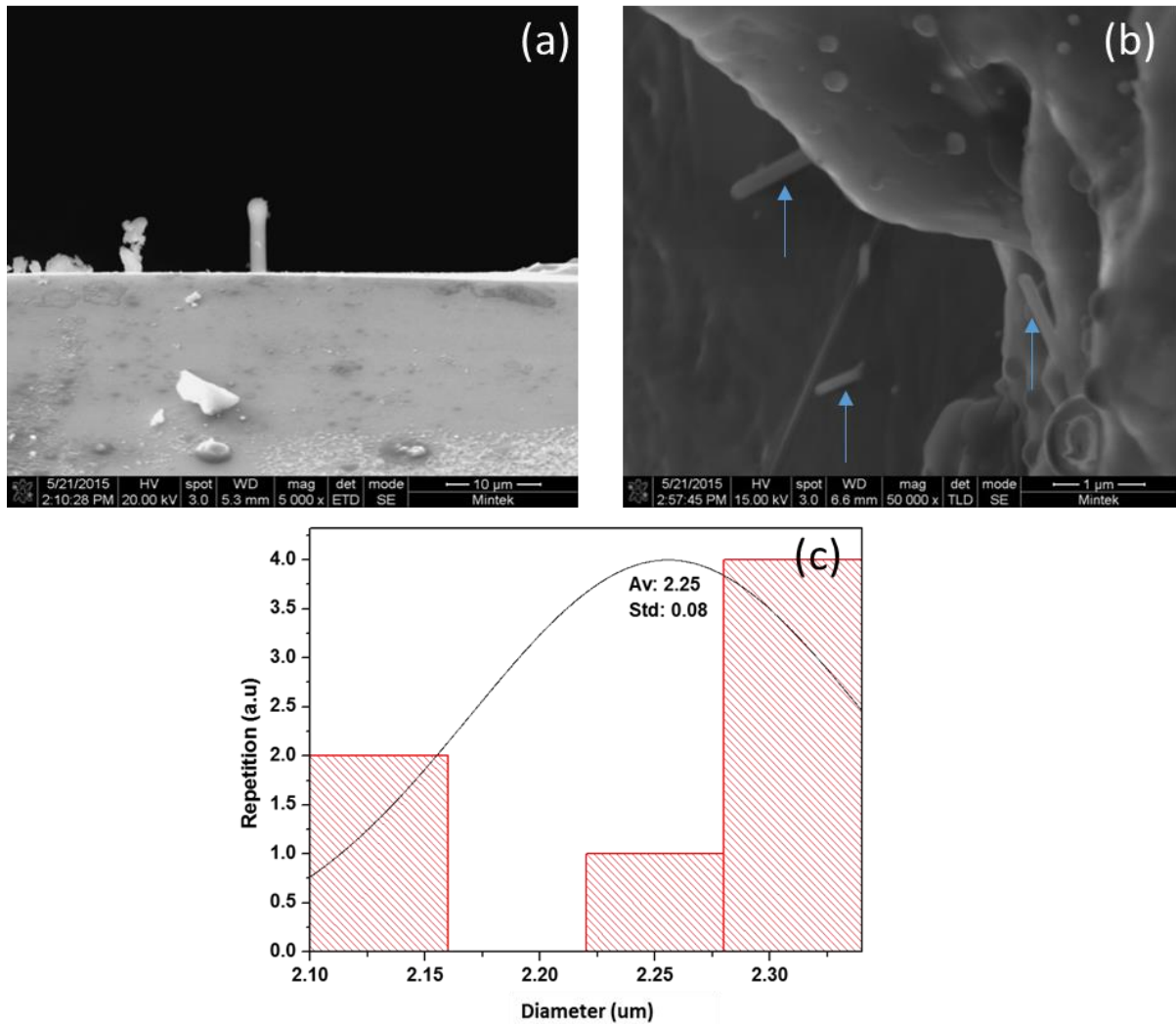


Figure 6.5: SEM images of SiNWs grown on a silicon wafer imaged from (a) silicon wafer cross section and (b) angle of 75° with a corresponding (c) particle size distribution histogram with a Gaussian curve fitted into the data.

Fig. 6.6 showed SEM image of AuNPs deposited on silicon wafer subjected to heat treatment at 1000°C for 30 minutes. The AuNPs have a wide particle size distribution ranging from nanometer to micrometer range. The growth was attributed to Oswald ripening and particles migration followed by coalescence as a result of heat treatment. This thermal energy activated the growth of AuNPs to form a polydispersed mixture. The use of such mixture as catalyst resulted in the formation of polydispersed SiNWs. This clearly suggests that the size of SiNWs is dependent on the size of AuNPs.

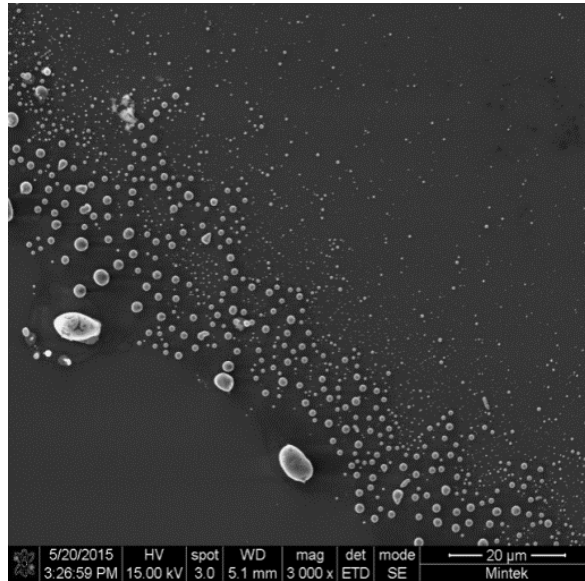


Figure 6.6: SEM image of gold particles on a silicon wafer after heat treatment to a temperature of 1000°C for 30 minutes.

6.3.2 Nickel Catalysed Silicon Nanowires

SEM image of nickel powder is shown in Fig 6.7. Nickel powder was made up of a mixture of small and big particles. The nickel particles ranged from 1 μm to 100 μm. The micron-sized particles appeared to have a monolithic structure with flat surfaces.

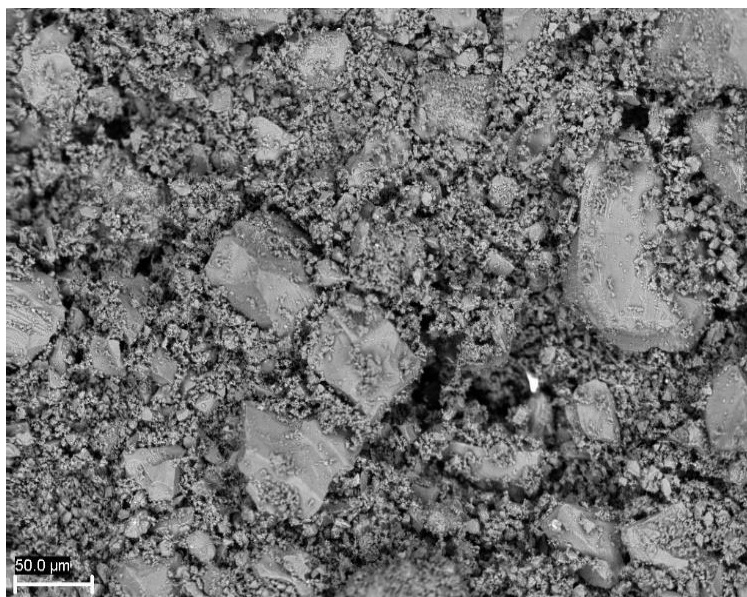


Figure 6.7: SEM image of nickel powder showing a mixture of relatively big particles with monolithic structure among relatively small particles.

Fig. 6.8 showed TEM image of SiNWs and particle size distribution histogram with a fitted Gaussian curve. The particle size distribution showed that SiNWs were 18 nm in average diameter with a relatively wider size distribution of 12 nm to 24 nm. Fig. 6.8 (a) showed a mixture of branched (marked as X) and unbranched (marked as Y) SiNWs which could be curved or straight. Several SiNWs appear to grow in different directions from the same nickel particle (marked as Z). Nickel-catalysed SiNWs are different from Au catalysed SiNWs in that Au catalysed SiNWs did not show branching and only one nanowire grew from the same Au particle. The formation of branched and unbranched SiNWs from the same particle probably relates to the nature and behaviour of nickel particle.

Nickel powder contains relatively big particles which could have produced more nickel atoms in the plume during laser ablation. The use of nickel particles as catalysts led to the formation of SiNWs with size distribution comparable to those generated in the presence of a gold catalyst. However, nickel particles were found to be relatively larger (Fig 6.7). The formation of SiNWs with uniform size is attributed to the oversupply of nickel atoms in the plume during laser ablation. More nickel atoms in the ablation plume could potentially have led to higher rates of atom clusters interconnection resulting in multiple nanowires from a single

metal particle (Fig. 6.8 (a) Marked as Z). The oversupply of nickel atoms also could have caused nanowire branching (Fig. 6.8 (a) Marked as X).

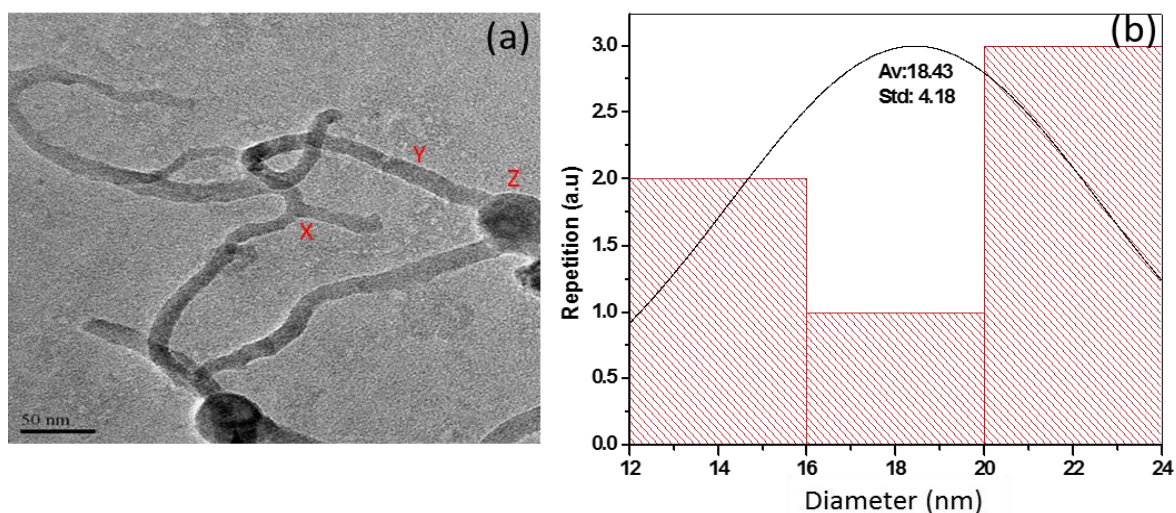


Figure 6.8: TEM image of (a) silicon nanowires and (b) size distribution histogram with Gaussian curved fitted into the data.

Fig 6.9 showed XRD pattern of SiNWs. XRD pattern showed the presence of sharp and narrow peaks suggesting a crystalline material. The peaks at 2-Theta values of 33° [111], 56° [220] and 67° [331] were all indexed to pure silicon, suggesting produced SiNWs were phase pure.

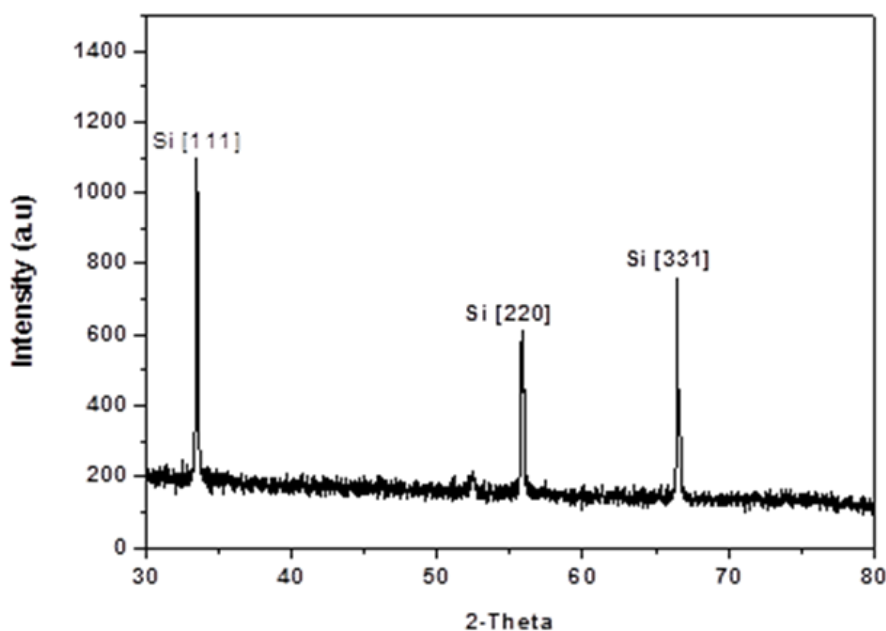


Figure 6.9: XRD pattern of nickel catalysed SiNWs prepared through laser ablation.

6.3.3 Mechanism of Formation of Branched and Interconnected Silicon Nanowires

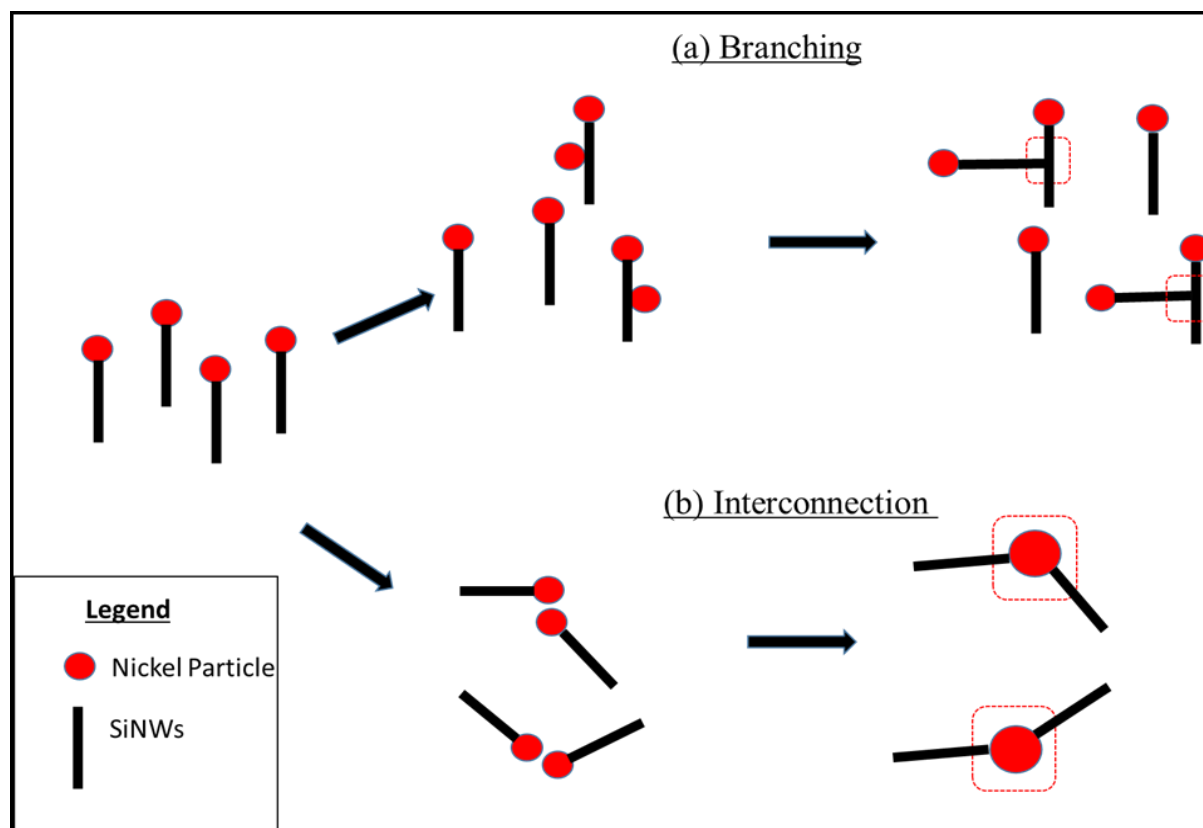
SiNWs synthesized using both nickel and gold catalysts were found to be 20 and 18 nm in diameter and are comparable. The size of nanowires grown from Au seems to depend on the size of the Au catalyst, whereas that of nanowires grown from Ni appears to be independent of the Ni catalyst size. This phenomenon suggests possible critical size of SiNWs independent catalyst size. However, earlier research has shown that laser breaks down the metal catalyst into a specific particle size depending on the laser energy. The formation of nanoparticles resulted from an increased collision and reduced mean path confined by laser plume [20]. In this study, laser delivered a total energy of 465 mJ, which seems to produce metal clusters with an average diameter of 20 nm. Hence, the formation of nanowires with the same size via VLS is irrespective of the starting catalyst size. XRD patterns of the SiNWs are similar in peak positions for both metal catalysts. It has been reported in the literature that catalysed SiNWs with sizes above 10 nm almost exclusively grow on [111] crystal plane, which is found to be the dominant plane in both the XRD patterns.

Nickel and gold catalysts used in this study showed significantly different particle sizes, Ni size was between 1 and 100 μm whereas Au was between 18 to 21 nm. Both catalysts tended

to conform to the VLS principles in the growth of SiNWs in that the catalyst particle absorbs Si atoms and crystallises them into nanowire form. However, Ni presents a unique growth where more than one nanowire grows from an individual catalyst. The multiple nanowires grown from a single nickel catalyst particle could be due to catalyst particle interconnection, where the molten catalyst particles coalesce forming a single but bigger particle as shown in Scheme 1. D. Dalacu *et al*, reported interconnection of nanowire metal tips to form a single particle with two nanowires [22]. This phenomenon was ascribed to a poor homogeneity of Ni incorporated silicon pellet relating to Ni catalysed SiNWs. Poor homogeneity of Nickel in the pellet could be due to the relatively bigger particles that could have been clustered. It is likely that Ni formed SiNWs through VLS and some Ni particles combined through interconnection to form multiple nanowires from a single particle shown in Fig. 6.8 (a) (Marked as Z). AuNPs were added to silicon powder to form a pellet which was then dried and mashed. It is highly unlikely that AuNPs could have been clustered in one spot of the pellet.

Branched SiNWs have been reported by Lieber *et al*, on gold catalysed SiNWs as; purging and re-introduction of silicon growth material [23]. During the purge step, the nanowire ceased to grow when the catalyst supersaturation levels significantly dropped which led to heterogeneous nucleation of a different crystal plane. Re-introduction of the growth material led to a nanowire growth with a different growth direction as shown in scheme 1. In this study, this could be possible since nickel/silicon has multiple eutectic points (1143°C and 966°C) depending on the amount of silicon absorbed by the nickel catalyst.

Scheme 1: Nickel catalysed silicon nanowires showing (a) branching and (b) interconnection.



Unbranched SiNWs are relatively inefficient in absorbing incident light for photovoltaic application. Even if the photon is absorbed the collected photocurrent is reduced due to various recombination processes. However, Branched SiNWs improve solar harvesting through an intense scattering of light that is not absorbed which leads to a longer path for light to travel through the absorber layer [24]. Synthesis of cheap branched SiNWs mostly includes sequential deposition of the metal catalyst followed by VLS. The whole process is repeated until the desired branching is achieved. In this study branched SiNWs were achieved by an in-situ constant supply of the Ni catalyst and the growth material from ablating the pellet for 30 minutes. This is a convenient and simple method of producing branched SiNWs with a metal catalyst.

6.4 Conclusion

SiNWs were successfully synthesized using Ni and Au catalysts by laser ablation. SiNWs grew through VLS mechanism. SiNWs synthesized using Ni catalysts were branched and grew in different directions from a single Ni catalyst which is due to catalysts interconnection and in-situ constant supply of catalysts. SiNWs diameter was controlled by the size of Au catalyst. There is a critical SiNWs diameter that is independent of the catalyst size when the catalyst is incorporated into the pellet. The laser breaks down catalyst particles to a specific atom cluster size which is depended on laser intensity. Branched SiNWs were achieved through an in-situ deposition of catalyst and growth material, which is more convenient and simple than most methods reported in the literature.

6.5 References

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Synthesis of Indium Phosphide Nanowires and their Application in Gas Sensors: TPD and DRIFTS Studies

7.1 Introduction

Group III-V semiconductor nanowires have attracted considerable attention due to their physical properties and potential application in nanoelectronics, optoelectronics [1-3] and sensors [4-5]. These properties are due to their superior electron mobility, structural flexibility and thermal stability [6-7] as well as the ability to carry charge and excitons efficiently. Indium phosphide nanowires are ideal building blocks for nanoscale high-power and high-frequency electronic devices [8]. However, lattice mismatch associated with the synthesis strategy leads to the formation of crystal dislocations and defects which can affect the performance of the device by reducing or inhibiting electron mobility [9-11]. In this study, we have set out to control the generation and distribution of dislocations and defects associated with indium phosphide nanowires. In order to keep the defect density low, modified chemical vapour deposition technique will be used to control the crystal structure, morphology and size distribution.

Various methods such as laser ablation [12], epitaxy [13], and furnace annealing [14-15] of In_2O_3 have been employed to control the crystal structure and morphology of indium phosphide nanowires, however, this remains a challenging feat. Chemical vapour deposition remains the simplest and most cost-effective method necessary for large-scale production of indium phosphide nanowires [14]. In this study, we report on the use of modified CVD where the residence time of the sample in the furnace is shortened to 15 mins while the system pressure is maintained between 500 mbar and 600 mbar. The possible formation mechanisms of the indium phosphide nanowires are discussed. Moreover, it is demonstrated that highly uniform and monodispersed indium phosphide nanowires can be grown using indium as the catalyst. The use of indium metalloid autocatalysis is advantageous in respect to InP crystal growth of phase purer product and elimination of separate catalyst preparation step.

Metal oxide semiconductors such as TiO_2 , ZnO , SnO_2 , amongst others, have interesting properties and have been widely used for gas sensing [16]. However, one-dimensional structures such as nanowires, nanotubes, quantum wires, etc. are considered as the most promising building blocks for nanoscale devices such as transistors and photodiodes [17-18]. Physical properties of InP nanowires along with large surface area-to-volume ratio and make them suitable for applications such as gas sensor [18].

In this work interaction between different analyte gases and the surface binding sites of InPNWs will be investigated using TPD and DRIFTS. Furthermore, the zinc blende crystal structure of the InP nanowires has been examined by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

7.2 Experimental Procedure

7.2.1 In-situ Synthesis and Growth of Indium Phosphide: Thermal Analysis Study

Phosphorus powder was mixed with indium or indium oxide powder (50 wt. % of each) using pestle and mortar to obtain a fine homogenous mixture. Using thermo-gravimetric analysis (TGA) the mixture was heated at $20^\circ\text{C}/\text{min}$ in argon atmosphere flowing at a rate of 50 sccm. TGA and differential scanning calorimetry (DSC) were measured simultaneously in-situ.

7.2.2 Synthesis of Indium Phosphide using Chemical Vapour Deposition

A mass of 40 mg of a homogeneous mixture of indium/phosphorus powder or indium oxide/phosphorus powder (50 wt. % of each) was achieved by using a pestle and mortar. After the samples were inserted into the chemical vapour deposition (CVD) furnace, it was then purged with argon at a flow-rate of 100 sccm for 10 minutes. After purging, the flow-rate was reduced to 50 sccm for the duration of the experiment. The precursors were heated isothermally at a heating rate of $20^\circ\text{C}/\text{minute}$ to a temperature between 300°C and 800°C and allowed a residence time between 15 and 30 minutes.

7.2.3 Monte Carlo Simulation

Monte Carlo simulation was carried out using Biovia material studio. The simulation predicted molecular adsorption of gases onto crystalline InPNW's [111] surfaces. An advanced simulation using adsorption locator was combined with structural modelling tools in the material studio desktop environment. This enabled understanding of the fundamentals of the sorption mechanism at the atomic level.

A gas kinetic theory was used to demonstrate the importance of the size of active sites in the adsorption of gases. Thermodynamic conditions were established using Kinetic Monte Carlo Simulations. Predictions of continuum approach and observations of the breakdown and limits of the continuum approximation as the size of active sites approach the mean free path of the gas: $L \rightarrow \lambda$ [10]. The InP crystalline size used for gas adsorption predictions was 4 atomic layers.

7.2.4 Temperature Programmed Desorption

A mass of 100 mg of InPNWs was purified using methanol prior to being used for TPD analysis. The sample was heated to 400 °C at a heating rate of 10 °C/minute in a helium atmosphere and then cooled to -50 °C at a heating rate of 5 °C/min using liquid nitrogen. Analyte gas mixture (5% of either CO or CH₄ in 95% helium) was allowed to flow through the sample momentarily with a contact time of 20 minutes at a flow-rate 10 sccm. The analyte gas was stopped and the sample was further purged with helium for 20 minutes at the same temperature at a flow-rate of 5 sccm. The sample was then heated to 350 °C at a heating rate of 5 °C/min under a constant flow of helium gas. The gas molecules desorbed from the sample were quantified by monitoring the mass balance of CO ($m/z = 28$) and CH₄ ($m/z = 8$) signals on the mass spectrometer.

7.2.5 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

Adsorption studies were carried out by passing analyte gas (5% of either CO or CH₄ in 95% helium) over the sample at a flow-rate of 20 sccm for 30 minutes. After the analyte gas was stopped helium gas was introduced into the cell at a flow-rate of 1 sccm while FTIR spectra were taken every 4 minutes as the CO gas was flushed out of the cell.

7.2.6 Gas Sensing Measurement

InPNWs were ultrasonicated in methanol for 5 minutes and an aliquot of 5 ml was drop-casted onto a patterned substrate with gold electrodes separated by 1 μm . The patterned substrate had heating electrodes on the rear side. The patterned substrate with the sample was placed inside the Kenosistec KSGAS6S instrument for electrical measurements. The measurements were all done in synthetic air.

7.3 Results and Discussion

7.3.1 Synthesis and Growth of Indium Phosphide

SEM images in Fig. 7.1 showed (a) indium metalloid powder (grey), (b) phosphorus powder (dark red) and (c) indium oxide powder (white). Indium metalloid particle shape was found to be spherical with a monolith structure and comprised of a mixture of relatively big particles (30 μm to 50 μm) and smaller particles (5 μm to 30 μm). Phosphorus particles were found to have irregular shapes with flat surfaces. Indium oxide particles were also found to have irregular shapes.

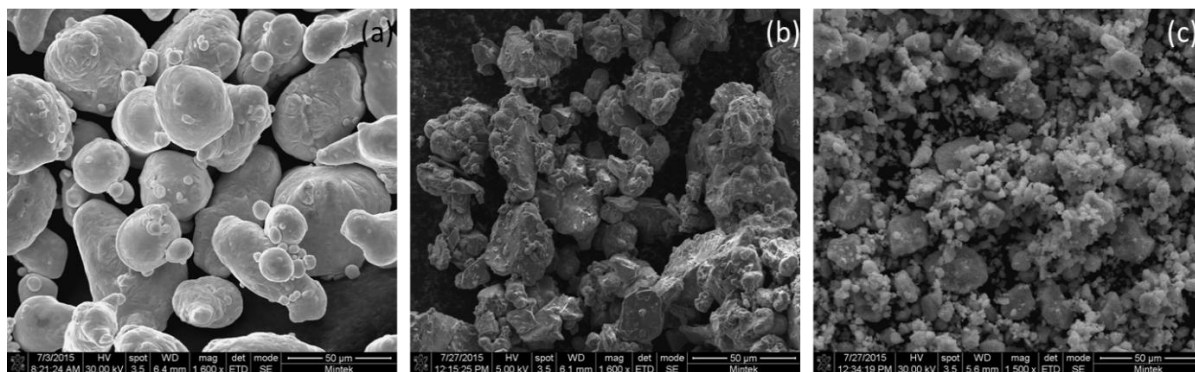


Figure 7.1: SEM images of (a) indium metalloid powder, (b) phosphorus powder and (c) indium oxide powder.

Fig 7.2 showed XRD patterns of (a) indium powder, (b) indium oxide powder and (c) phosphorus powder. The XRD patterns of indium and indium oxide both showed sharp and narrow peaks suggesting a crystalline material. XRD pattern of indium powder showed peaks at 2-theta values of 38° [101], 42° [002], 64° [112], 66° [200], 74° [103] and 79° [211] and

were all indexed to pure indium with a tetragonal structure. XRD pattern of indium oxide showed peaks at 2-theta values of 34° [211], 36° [222], 42° [431], 60° [440] and 72° [444] which were all indexed to indium oxide (JCPDS, Card No. 4-784). Phosphorus was found to have a broad peak which is characteristic of an amorphous material.

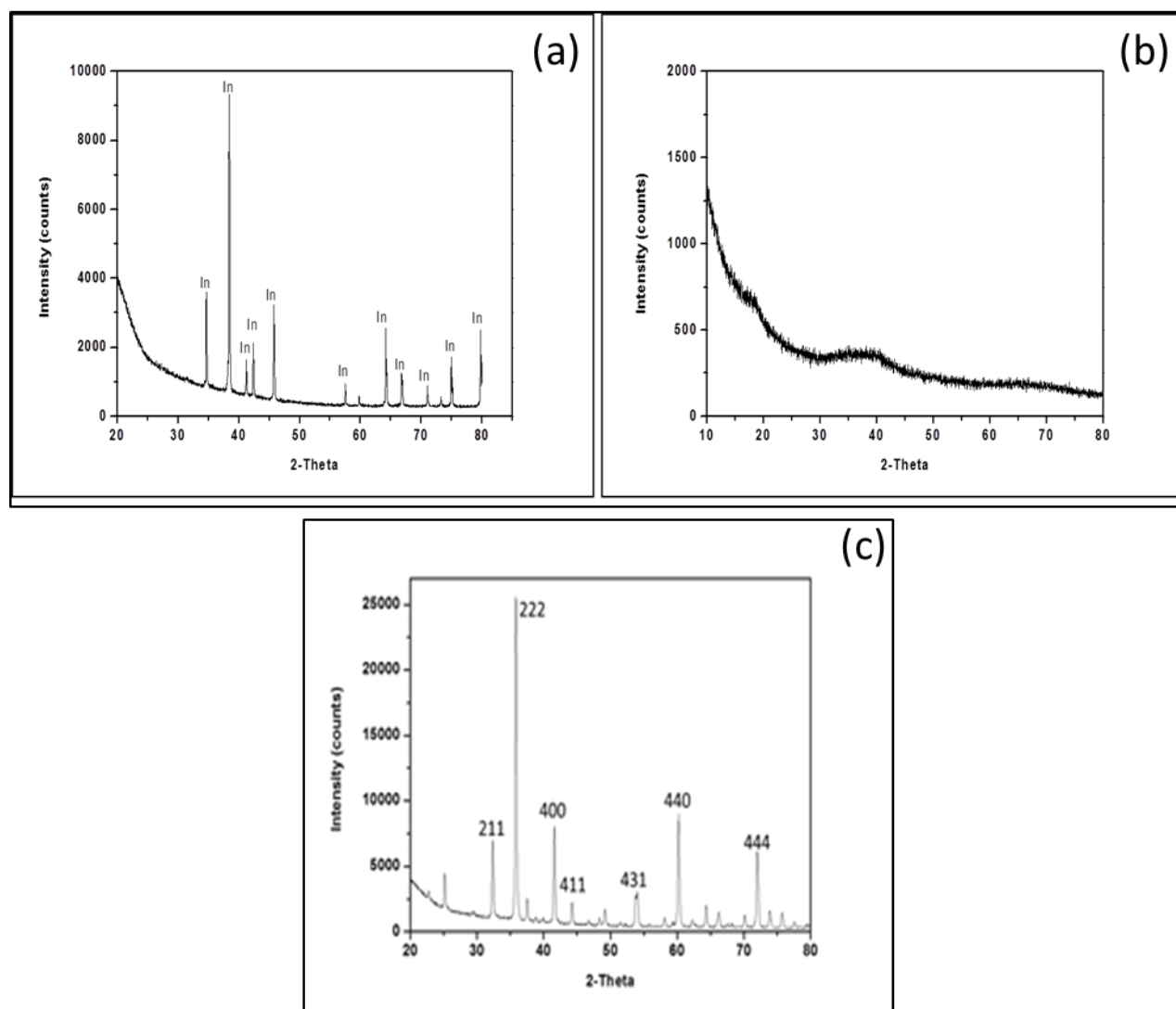


Figure 7.2: XRD patterns of (a) indium powder, (b) indium oxide powder and (c) phosphorus powder.

7.3.1.1 In-situ Synthesis of InP through Simultaneous Thermal Analysis (STA)

Fig. 7.3 (a) showed thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) graphs of indium metalloid and phosphorus mixture and Fig. 7.3 (b) showed STA of a

mixture of indium oxide and phosphorus. DSC graph of a mixture of indium metalloid and phosphorus powders showed a decrease in energy at a temperature of 150°C and another one at a temperature between 400°C and 500°C. A decrease in energy in both cases was attributed to the melting temperature of both indium metalloid and phosphorus [19]. The melting temperature predicted from the DSC graph is comparable to the literature values which are 158°C for indium metalloid and 400°C for red phosphorus [19-20]. DSC graph showed a crystallisation peak at a temperature range of 500°C to 600°C and this was attributed to the formation of a crystalline phase. TGA of a mixture of indium and phosphorus showed that at a temperature of 149°C (indium melting temperature) there was no observable weight loss, but at a temperature of 400°C (phosphorus melting temperature) there was 25% weight loss. The weight loss observed from TGA graph at 400°C was attributed to phosphorus moderate volatility.

DSC graph of a mixture of indium oxide and phosphorus showed a change in thermal energy at a temperature between 450°C and 500°C and TGA showed a mass loss of 35% at the same temperature range. The changes in energy and weight loss were also due to loss of phosphorus at that temperature. Crystallisation peak was observed at a temperature between 500°C and 600°C. Crystallisation peaks of indium oxide and phosphorus mixture and indium and phosphorus mixture systems both occurred at a temperature range of 500°C to 600°C.

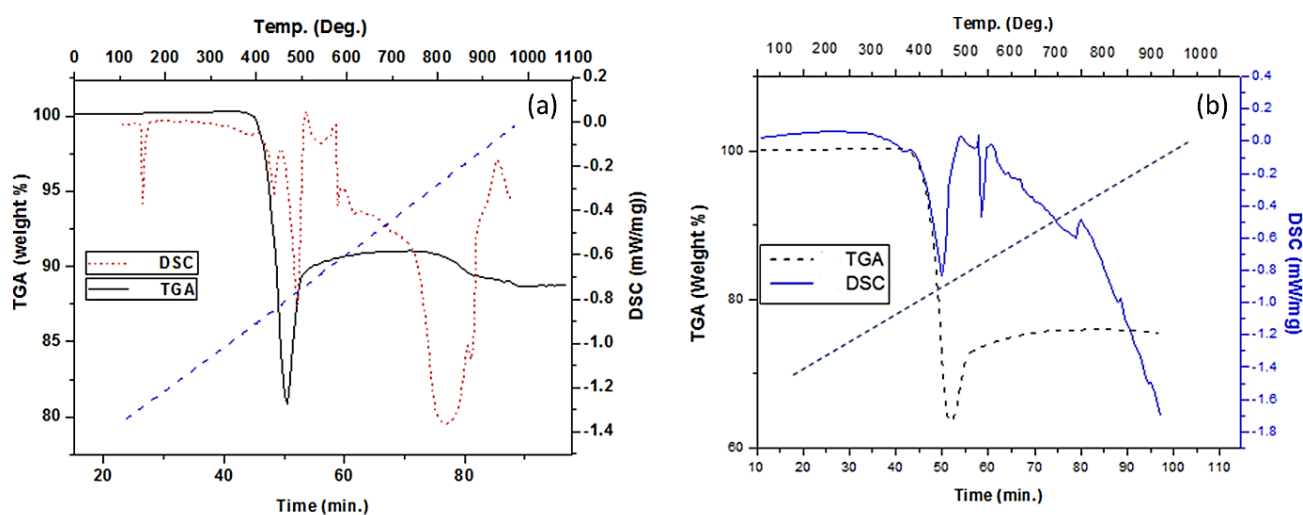


Figure 7.3: Simultaneous thermal analysis spectra for mixtures of (a) indium metalloid and phosphorus and (b) indium oxide and phosphorus.

7.3.1.2 Physical Properties of Indium Phosphide Synthesized through Indium Oxide and Phosphorus Reaction

XRD patterns shown in Fig. 7.4 are of a mixture of (a) pristine indium oxide and amorphous phosphorus and product synthesized by processing the mixture at (b) 500°C and (c) 600°C. XRD pattern of pristine indium oxide and phosphorus mixture revealed the presence of sharp and narrow peaks at 2-theta angles of 34° [211], 36° [222], 42° [431], 60° [440] and 72° [444] which could be indexed to indium oxide. Thermal treatment of indium oxide and phosphorus mixture at 500°C and 600°C led to the formation of new phase as evidenced by the emergence of new relatively broader peaks at 2 Theta values of 31° [111], 52° [311] and 61° [400] which could be indexed to indium phosphide.

The phase change observed from XRD patterns occurred between a temperature of ~450°C and 600°C, which was consistent with STA results that showed a crystallisation peak at a temperature range of 450°C to 600°C.

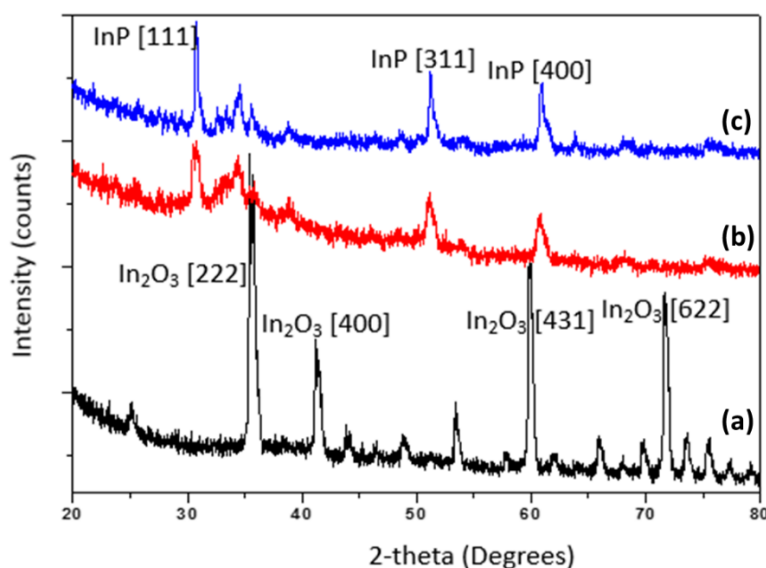


Figure 7.4: XRD patterns of (a) indium oxide and phosphorus mixture used to synthesise indium phosphide at a temperature of (b) 500°C and (c) 600°C.

The products obtained from heating indium oxide and phosphorus mixture at 500°C and 600°C are shown in the SEM images in Fig. 7.5 (a) and (c). The particle size distribution histograms of InP synthesized at 500°C and 600°C are shown in Fig. 7.5 (b) and (d). The

SEM images revealed that the material processed at 500°C and 600°C were made up of nanowire structures. InPNWs produced at 500°C were found to be straight with an average diameter of 600 nm and a relatively wide particle size distribution between 200 and 1200 nm. InPNWs synthesized at 600°C were also found to be straight with an average diameter of 900 nm and relatively narrow particle size distribution between 600 nm and 1400 nm. InPNWs synthesized at both 500°C and 600°C were found to have a darker spherical tip, which was confirmed to be indium by means of EDX results. Nanowire with a metal tip is typical for SLS and VLS mechanisms for the growth of nanowires. Indium metalloid acted as both growth material and a catalyst material. Since the melting point of indium metalloid (200°C) is lower than that of InP (1060°C) makes the growth mechanisms a SLS mechanism.

In a typical SLS mechanism indium metalloid melted into metal liquid droplets. The metal droplets absorbed the phosphorus and indium atoms forming a liquid alloy droplet to a point of supersaturation. At the supersaturation of the metal alloy, precipitation of InP material occurred which led to an axial growth of InPNWs. Prolonged growth led to the formation of elongated InPNWs [21].

InPNWs average diameter increased from 600 nm to 900 nm when the synthesis temperature was increased from 500°C to 600°C. The InPNWs growth was attributed to a formation of relatively bigger nuclei due to higher thermal energy from the furnace heat during indium catalyst crystallisation. The larger liquid indium nuclei produced InPNWs with relatively bigger diameters during axial growth.

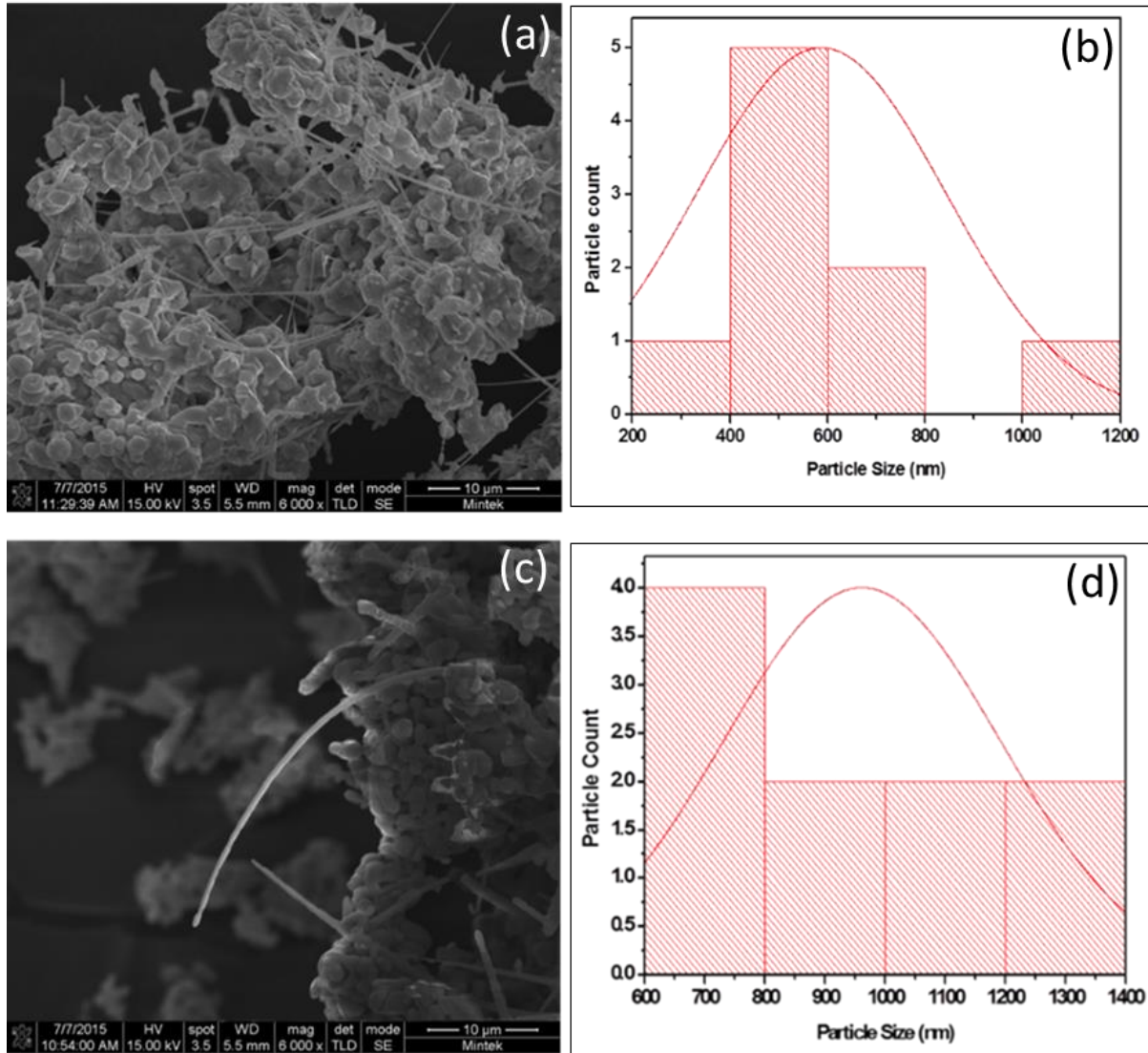


Figure 7.5: SEM image of indium phosphide nanowires synthesized at a temperature of (a) 500°C and (b) size distribution, as well as SEM image indium phosphide nanowires processed at (c) 600°C with (d) particle size distribution histograms.

TEM images of InPNWs synthesized at a temperature of 500°C and 600°C are shown in Fig 7.6. TEM images showed that InPNWs contained surface defects evidenced a segmented surface. InPNWs processed at 600°C (Fig. 7.6 b) contained branched segments that were relatively distributed evenly compared to the InPNWs processed at 500°C. Branching was attributed to the SLS growth mechanism the InPNWs. In a typical SLS growth mechanism, a catalyst melting temperature is lower than that of the nanowire. This difference in melting temperatures caused the indium and phosphorus alloy to precipitate InP phase at intervals

which led to segmented InPNWs. This type of growth was reported by Y. Yu *et al* [15], where they suggested that the bamboo-structure was formed through the formation of knots, where when the growing knot reaches certain thickness a twin plane is formed which halts the growth of the InPNW. Halting of the knot shifts and reverses its growth direction giving birth to a new knot, which gave the nanowire a bamboo structure. The reason for well-defined knots in InPNWs synthesized at 600°C was due to high thermal energy causing higher atom migration compared to 500°C.

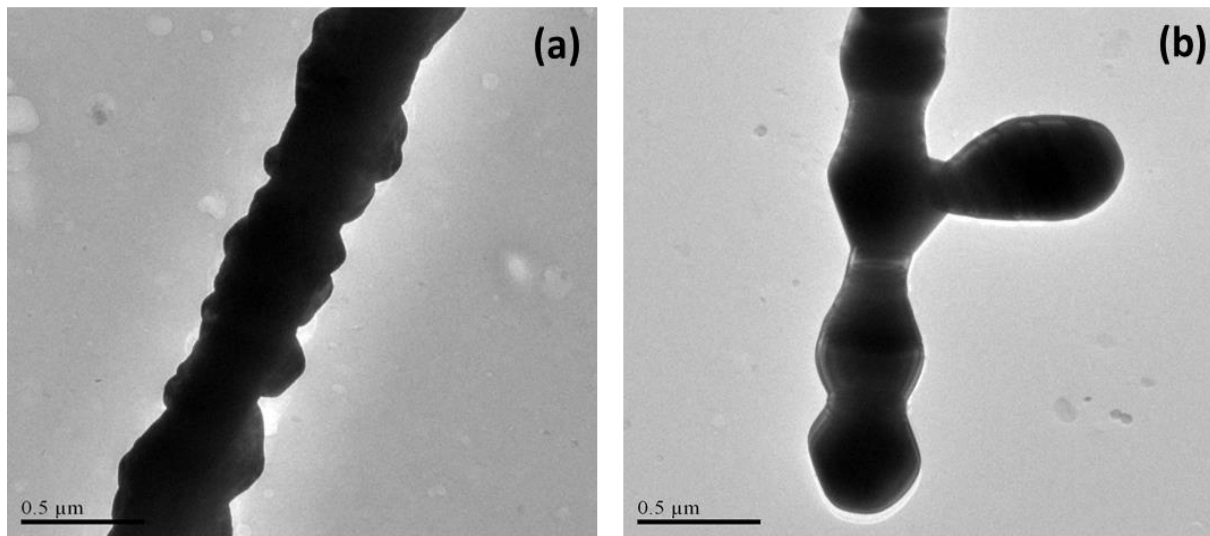


Figure 7.6: TEM images of InPNWs processed at (a) 500 °C and (b) 600 °C.

HRTEM micrographs of InPNWs processed at 500°C are shown in Fig 7.7. HRTEM images showed horizontal (Fig 7.7 a) and diagonal (Fig 7.7 b) lattice fringes with respect to the growth direction of the InPNW. The same phenomenon was observed for InPNWs prepared at 600°C (not shown). In general, segmented InPNWs are known to deteriorate the electrical mobility of nanowires due to electron transport hindrance at the segment boundaries [22].

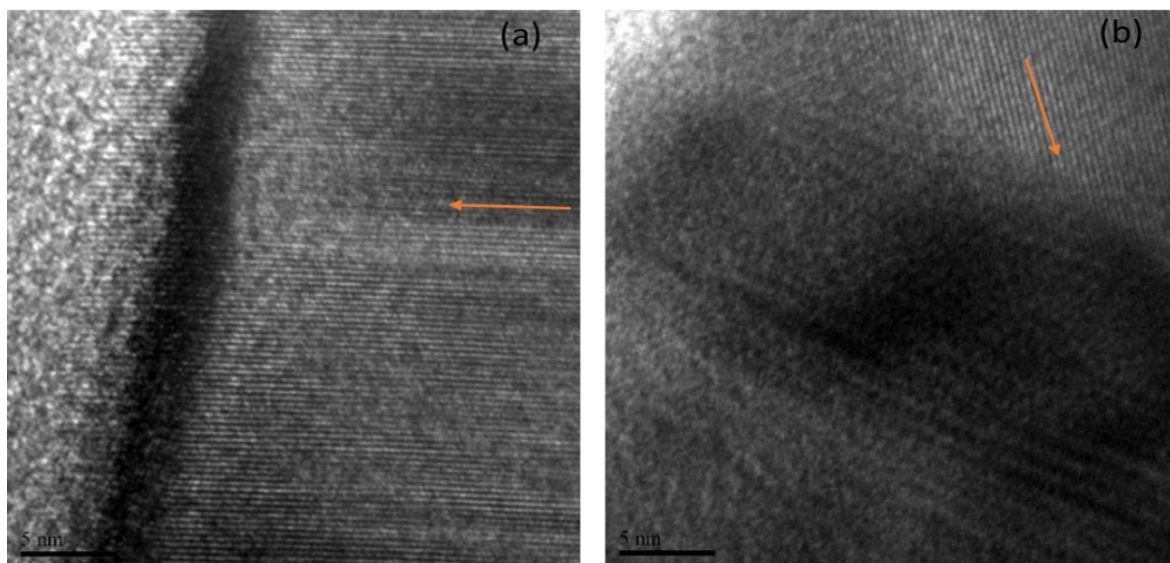


Figure 7.7: HRTEM images of InPNWs synthesized at 500°C showing (a) horizontal and (b) diagonal lattice fringes.

7.3.1.3 Structural Properties of Indium Phosphide Synthesized through Reaction of Indium metalloid and Phosphorus

XRD pattern of the samples processed at 500°C and 600°C are shown in Fig 7.8. The samples both contained peaks at 2-theta angles of 31° [111], 52° [220], 61° [311] and 72° [400] which could be indexed to InP phase. The peaks at 2-theta angles of 38° [202] and 64° [006] were indexed to In₃P.

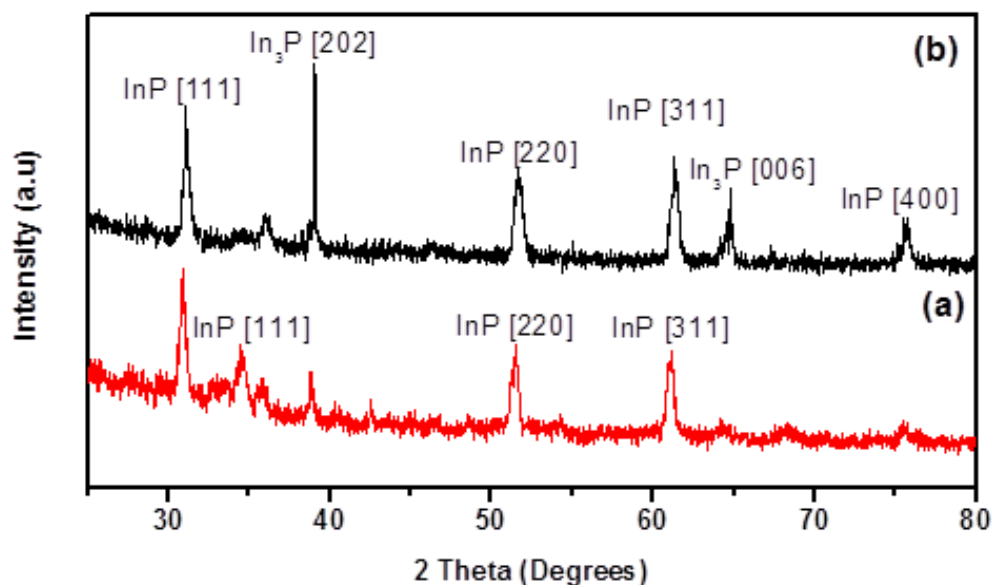


Figure 7.8: XRD pattern of the samples processed temperatures of (a) 500°C and (b) 600°C.

In order to investigate the origin of In_3P phase, synthesis of other samples from the reaction of indium metalloid and phosphorus at lower temperatures (300°C and 400°C) was carried out and analysed. XRD pattern of the samples prepared at temperatures of 300°C and 400°C are shown in Fig 7.9. XRD pattern of the sample prepared at 300°C (Fig. 7.9 a) showed a single peak at a 2-theta angle of 38° and it corresponded to In_3P [202] crystal plane. XRD pattern of the sample prepared at 400°C showed peaks at 2-theta angles of 38° [202], 43° [113], 46° [104], 65° [006] and 67° [223] and could be indexed to In_3P phase. XRD results of the samples prepared at temperatures of 300°C and 400°C clearly showed that rhombohedral In_3P phase was formed at lower temperatures. The In_3P phase was thought to be an intermediate phase which transformed to InP when the temperature was elevated

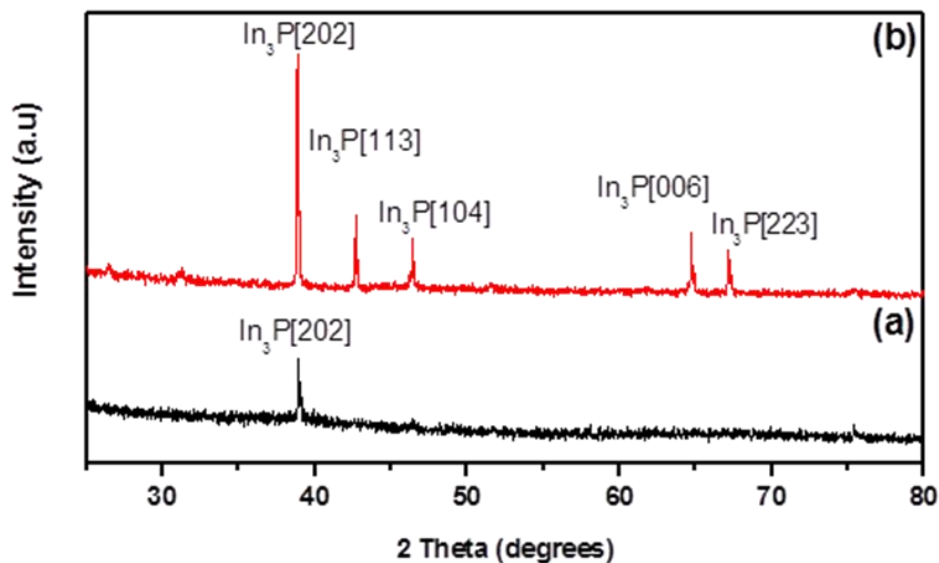


Figure 7.9: XRD patterns of samples processed at a temperature of (a) 300°C and (b) 400°C.

Phase purification of InP synthesized at 600°C was achieved by heat treatment at 100°C for 24 hours which eliminated the intermediate In_3P phase shown in Fig 7.10 insert. XRD pattern for purified InP prepared at 600°C is shown in Fig. 7.10. InP prepared at 600°C showed narrow and sharp peaks at 2-theta angles of 31° [111], 52° [220], 61° [311] and 72° [400] without any of the In_3P phase. The phase pure InP prepared at 600°C were used for all the testing shown in subsequent sections.

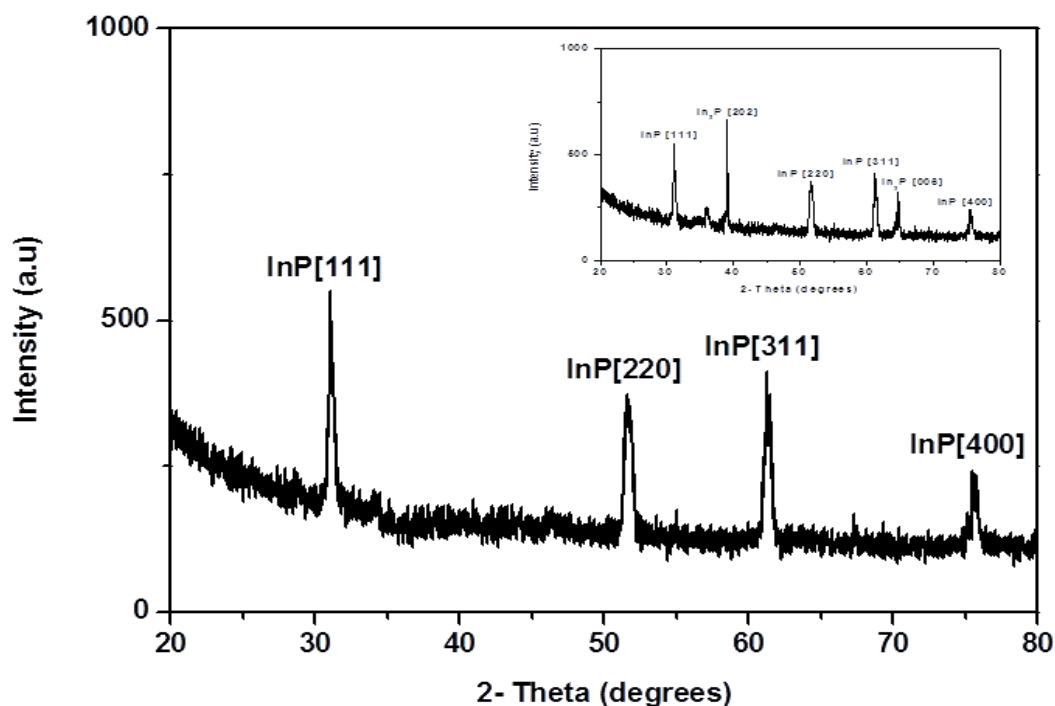


Figure 7.10: XRD spectrum for purified InP synthesized at 600°C and insert showing phase impure InP.

InP synthesized from the reaction of indium metalloid and phosphorus at a temperature of 500°C and 600°C are shown in the SEM images in Fig. 7.11 (a) and (c) with their respective EDX spectra shown in Fig. 7.11 (b) and (d). Both the samples showed InP in a nanowire form as well. InPNWs synthesized at 500°C had an average diameter of 1100 nm and length between 2 μm and 2.5 μm . EDX spectrum of InPNWs synthesized at 500°C showed peaks of indium and phosphorus which could be confirmed to be InP from XRD pattern of the same sample (Fig. 7.10). InPNWs synthesized at 600°C had an average diameter of 80 nm and length between 3 μm and 5 μm . EDX spectrum showed that the sample was composed of indium and phosphorus.

InPNWs synthesized at both 500°C and 600°C appeared to have grown off indium particle substrate. The InPNWs diameter decreased while length increased when the temperature was increased from 500°C to 600°C. The increase in the length of InPNWs was attributed to prolonged growth driven by thermal energy at a higher temperature.

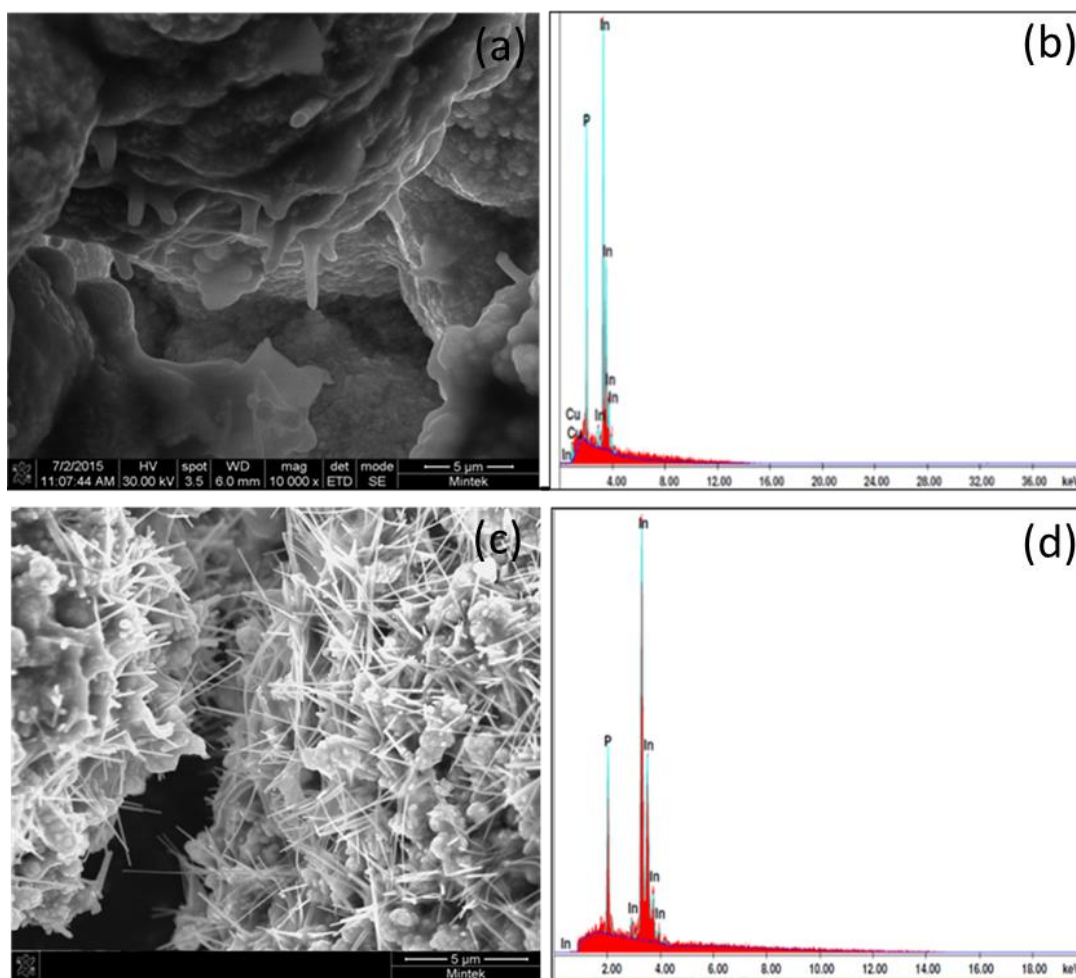


Figure 7.11: SEM images of InPNWs prepared at (a) 500 °C with corresponding (b) EDX spectrum as well as SEM image of InPNWs prepared at (c) 600 °C with corresponding (d) EDX spectrum.

Figure 7.12 showed Raman spectra of samples produced at 400 °C, 500 °C and 600 °C. Raman spectra showed two peaks at 300 cm^{-1} and 348 cm^{-1} for both the samples. The peak position is characteristic of bulk InP transverse and longitudinal optical phonons. Raman was used as a qualitative confirmatory tool for the formation of InP phase. Raman results confirmed the formation of InP phase and this was in agreement with XRD results (Fig. 7.10).

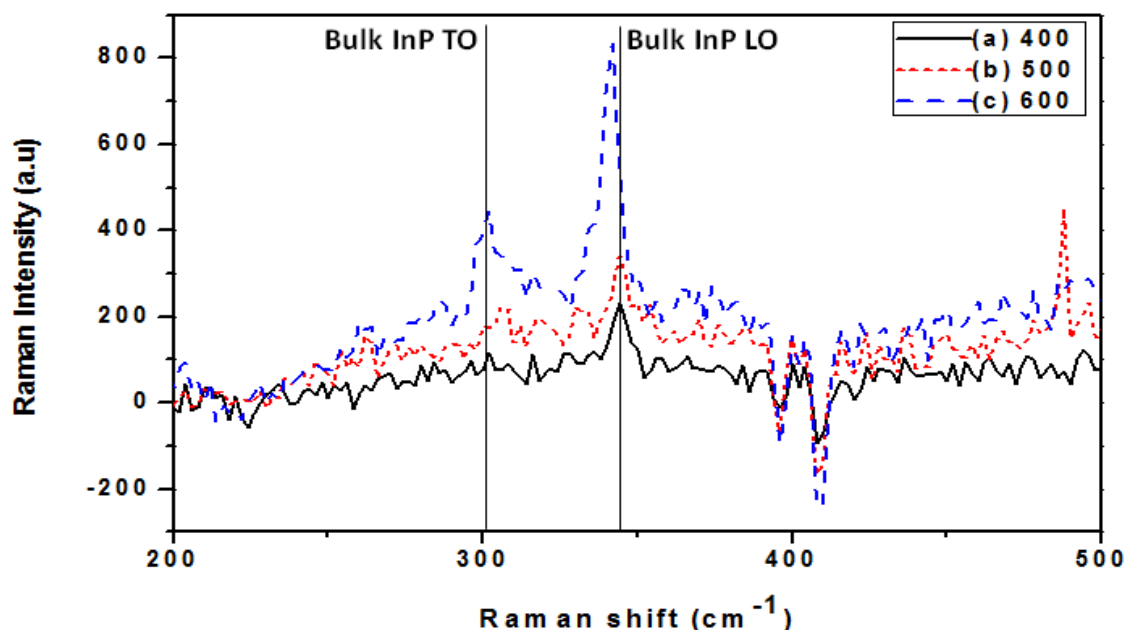


Figure 7.12: Raman spectra of the InPNWs produced at (a) 400 °C, (b) 500 °C and (c) 600 °C.

TEM image of InPNWs processed at 600 °C are shown in Fig 7.13 (a). The TEM image showed the presence of particles with a nanowire structure. The sample processed at 600 °C produced InPNWs with the desired morphology and dimensions and as such, this is considered an optimised sample. TEM images revealed that the InPNWs were segmented with dark lines across and these are considered structural defects better known and understood as stacking faults [23]. The stacking faults are a common phenomenon for group III-V semiconductor nanowires and are associated with disordered crystals. This phenomenon could have an adverse effect on electronic mobility in the nanowires [23]. Controlling stacking faults is imperative in an attempt to improve III-V semiconductor nanowires electron conductivity. AFM image in Fig 7.13 (b) showed that the InPNWs length was between 3 μm to 5 μm .

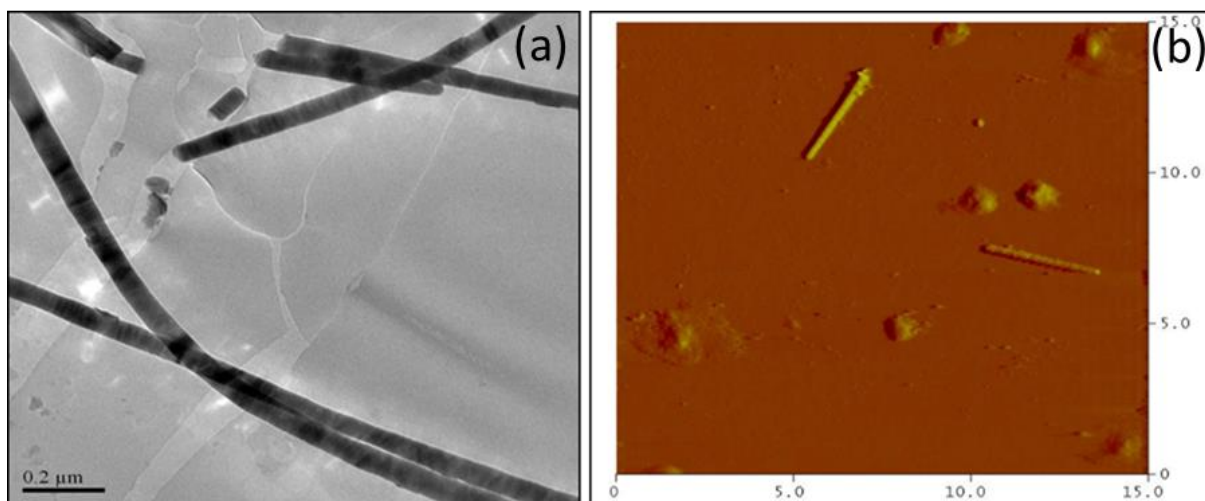


Figure 7.13: TEM image of (a) InPNWs processed at 600°C and (b) atomic force microscope image of the same sample.

HRTEM image of InPNWs in Fig. 7.14 showed crystal planes or fringes across InPNWs. The SAED spectrum in Fig 7.14 (a) insert showed that the fringes were due [111] crystal plane growth. Fig. 7.14 (b) showed that fringes did not change direction at the fault boundary.

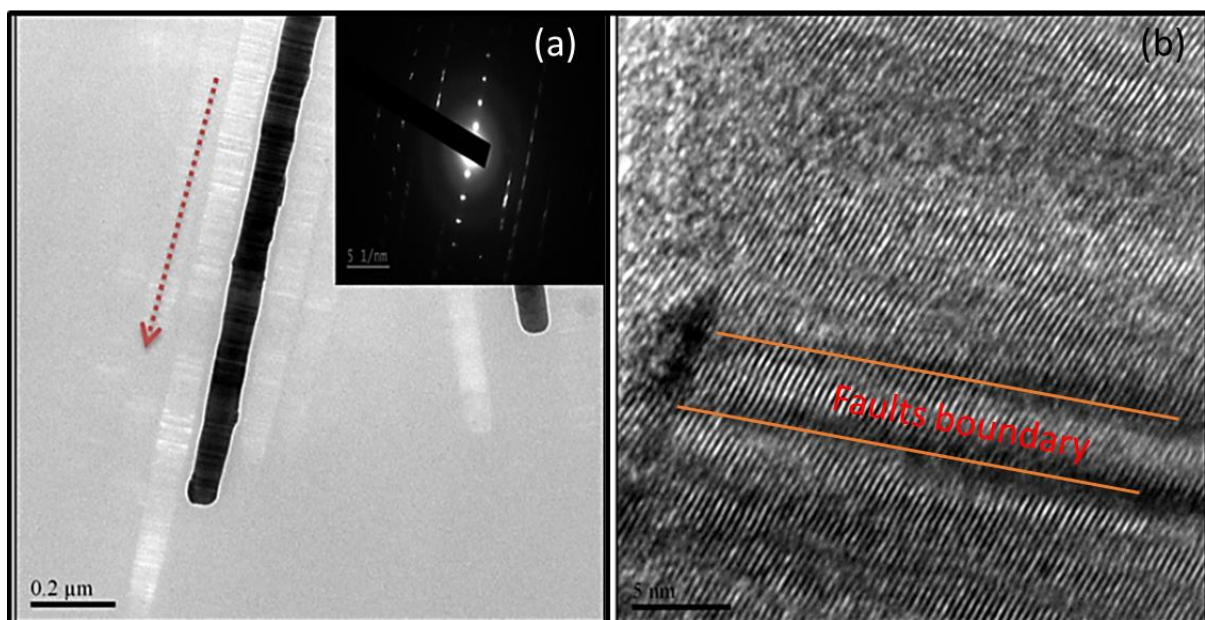


Figure 7.14: High-resolution TEM images of indium phosphide nanowires showing (a) crystal planes and (b) spatial interface.

Zinc blende and wurtzite are typical polymorphs for some group III-V semiconductors. As such both these polymorphs have been reported to experience polytypism. Polytypism is a phenomenon where both polymorphs exist in a material. The zinc blende and wurtzite motifs grow in different crystal directions. Thus, zinc blende grows along the [111] crystal plane while wurzite grows along the [001] crystal plane. Polytypism is characterised by fringes changing directions at fault boundaries.

The d-spacing was measured to be 0.342 nm using FFT on ImageJ software as shown in Fig. 7.15. The measured d-spacing is comparable to that of known spacing between two [111] crystal planes (0.340 nm) of zinc blende structure [24]. The d-spacing results suggest that fringes parallel to the growth direction of the nanowires are due to growth along [111] crystal planes. The d-spacing information and selected area electron diffraction (SAED) both suggests that the dominant crystal plane of the InPNWs was [111]. This study, showed that InPNWs grew with a zinc blende structure and the wurtzite phase was suppressed during crystal growth. The presence of a single motif has a potential to improve the nanowire's electrical properties.

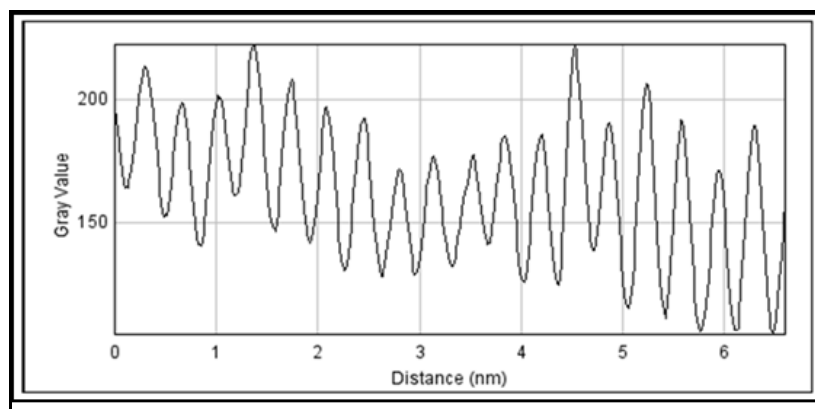


Figure 7.15: The d-spacing measurements of InPNW using FFT image.

The 2θ angle due to the d-spacing obtained from the HRTEM can be determined using Bragg's equation (Equation 1).

$$n\lambda = 2d\sin\theta \dots \dots \dots \text{Equation 1}$$

Where n is a positive integer 1, d is the d-spacing and λ is the wavelength of the X-rays, which depends on the source used. In this study a cobalt source was used with a λ of 1.78897 Angstroms. By substituting the calculated d-spacing of 0.342 nm, the 2θ angle could be calculated to be 31° and this corresponded to the InP [111] peak on the XRD pattern (Fig. 7.10).

The specific surface area and total pore volume of InPNWs were measured to be $137 \text{ m}^2/\text{g}$ and $0.31 \text{ cm}^3/\text{g}$ respectively using Brunauer-Emmett-Teller (BET).

7.3.2 Electrical Properties Measurements

7.3.2.3 Fabrication of Multiple InPNW-based two Terminal Device using Di-Electrophoresis

The SEM image of a two terminal InPNW-based device is shown in Fig. 7.16. The two gold electrodes were connected by InPNW. The InPNW could not be well anchored on the electrodes since it relies on weak van der Waals forces, a typical phenomenon for DEP fabrication. InPNW used in this work were synthesized at a temperature of 600°C and were purified using methanol and heat treatment.

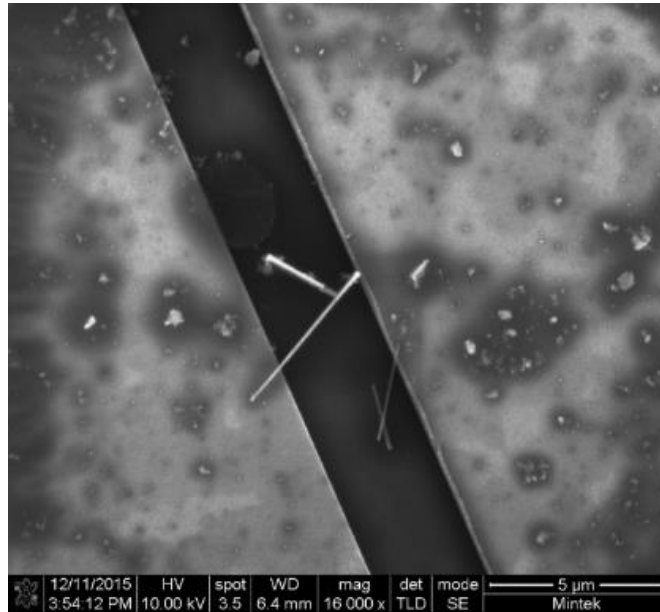


Figure 7.16: SEM image of a two terminal InPNW-based electronic device fabricated using dielectrophoresis.

Current-voltage curve of the InPNW-based device is shown in Fig. 7.17. The InPNW based device showed that as the applied voltage was varied, the electrical current passing through the InPNW was also varied. Even though the InPNWs were not well anchored to the electrodes but electrical measurements could be done. Current-voltage curve shape of InPNW was characteristic of that of a transistor, where the electric current increases exponentially when the voltage is applied. In the absence of InPNWs, the electrodes did not conduct electrical current when the voltage was applied suggesting that silicon oxide layer used to passivate silicon substrate eliminated electrical current leakage. InPNW-based device current-voltage curve showed that electrical current could flow in both directions of the nanowires with a measured resistivity of $50 \Omega \cdot \text{cm}$. The flat region at low voltage was due to electron barrier resulting from electronic band gap or mismatched work functions of InP and gold.

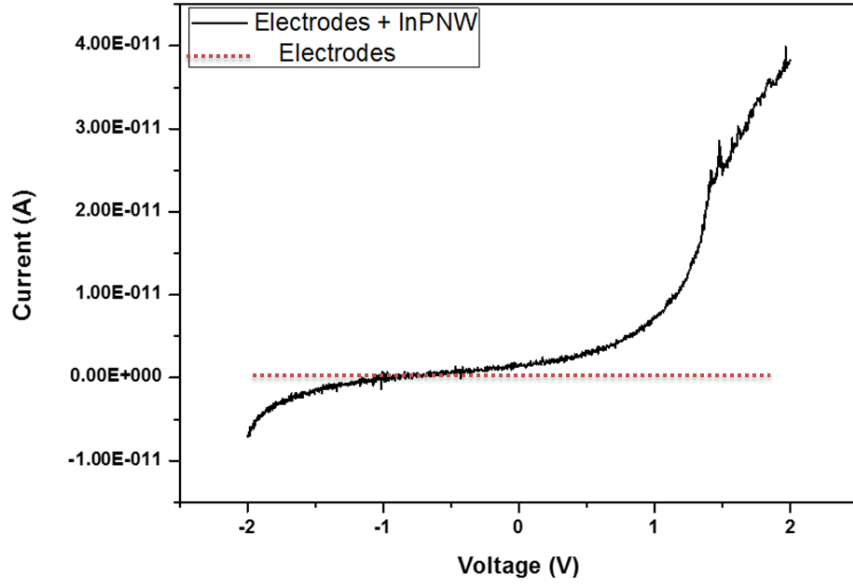


Figure 7.17: Current-voltage curve of InPNW two terminal device fabricated using DEP.

7.3.2.4 Fabrication of Single InPNW-based two Terminal Device using Electron Beam Lithography

In this section fabrication of two terminal electrical single InPNW-based devices (Fig 7.18) and its incorporation into a back-gated field effect transistor whose electrical properties are characterised is reported. As isolated InPNW used for the fabrication of the device was 1.2 μm in length and 90 nm in diameter.

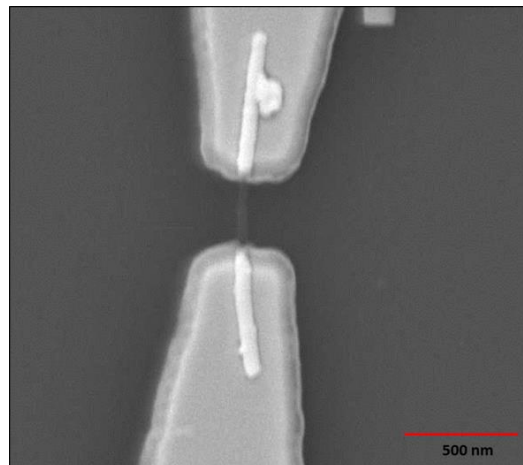


Figure 7.18: SEM image of indium phosphide based single nanowire electronic device with Au electrodes.

Current-voltage curves of the single InPNW-based electrical device and material density of states (DOS) are shown in Fig. 7.19. Similar to the DEP fabricated InPNWs-based electrical device, the current-voltage curve showed that electrical current can flow in both directions (Fig.7.19 a). In order to experimentally estimate the band gap using I-V curves, low-temperature studies needed to be carried out. The InPNW resistivity was calculated to be 50 Ω .cm. This was obtained by extrapolating a straight line from a 20V to 40V part of the I-V curve of Fig.7.19 (a). The resistivity is the slope calculated from the extrapolated straight line. Due to a small change in electrical current, the density of states (DOS) could not be determined from the dI/dV curve as shown in Fig. 7.19 (b).

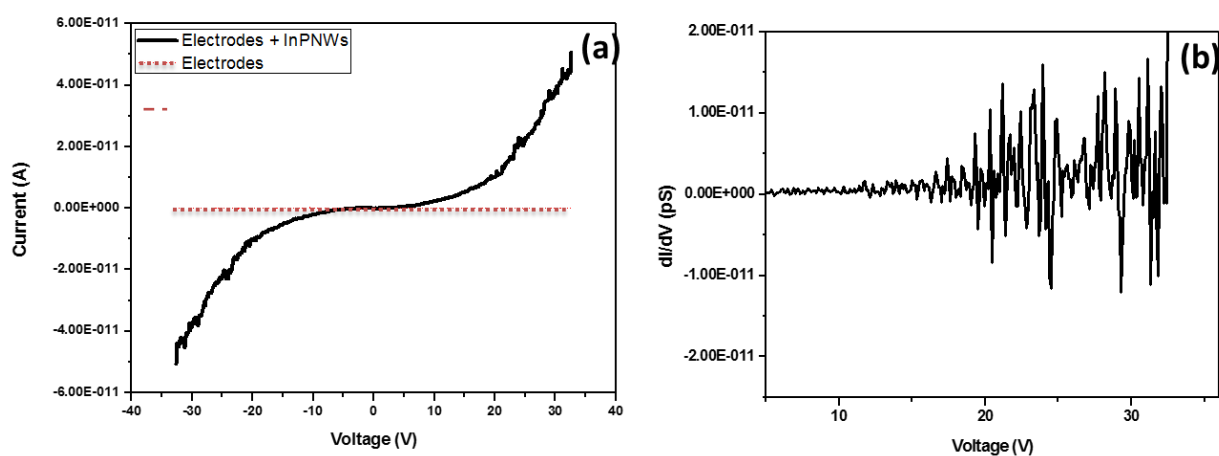


Figure 7.19: (a) Current-voltage curve of the indium phosphide nanowires device (b) local density of states (dI/dV) of InPNWs electronic device.

The electrical measurement of the InPNW-based electrical device revealed that the CVD synthesized InPNWs could conduct electric current, regardless of the high density stacking faults found in their structure. Stacking faults nature and low density can be achieved by using sufficiently low growth rates. HRTEM image of the InPNWs in Fig. 7.14 showed that the crystal planes were parallel to the growth direction suggesting uninhibited flow of electrons hence uncompromised electrical current flow.

7.3.3 Indium Phosphide Nanowires Gas Adsorption Studies: TPD and DRIFTS

7.3.3.1 Temperature Programmed Desorption (TPD) Analysis

A typical desorption TPD profile of CO and CH₄ gases on InPNWs is shown in Fig 7.20. The temperature at which the M/Z signal (rate of desorption) was maximum (T_{max}) was found to be 239 °C for CO and -33 °C for CH₄. Desorption of the gases was found to occur between 220 °C to 260 °C for CO and -45 °C to -15 °C for CH₄. The desorption profiles of both the gases showed the presence of a single peak suggesting that interaction between the gases and InPNWs occurred through the same set of binding sites. TPD analysis of the analyte gases (CO and CH₄) was done to determine the binding characteristics of the analyte gases with the binding sites of InPNWs. The T_{max} values extrapolated from desorption profiles were used to calculate the desorption enthalpy.

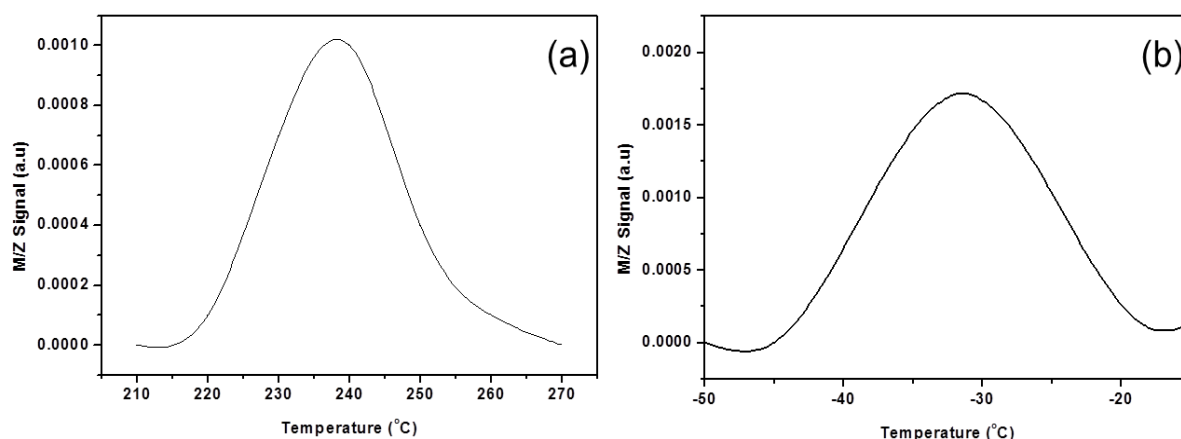


Figure 7.20: TPD profiles showing a single peak for both (a) carbon monoxide and (b) methane gases.

Desorption enthalpy was calculated using the Redhead method [25].

$$\frac{E_d}{RT_p} = \ln \left\{ \frac{vT_p}{\beta} \right\} - 3.64 \dots \dots \dots \text{Equation 7.2}$$

Where E_d is the desorption enthalpy, T_p is the temperature at maximum desorption rate, β is the heating rate, and v is the frequency factor approximated, for first-order kinetics, to be 10^{13} s^{-1} . The calculated desorption enthalpy was found to be 142 kJ/mol for CO and 38 kJ/mol for

CH₄. Desorption enthalpy above 50 kJ/mol is known to be due to chemisorption and below is due to physisorption [19, 26]. This indicates that CH₄ physically adsorbed on the surface of InPNWs through weak van der Waals interaction. The results also indicated that electron transfer between the CO and InPNWs led to a chemical bond formation. Each CO binding mode (linear or terminal, 2f hollow bridging and 3f hollow) has desorption enthalpy associated with it and this increases from linear, 2f hollow bridging to 3f hollow bridging respectively. TPD results revealed the interaction between InPNWs and CO to be chemisorption and that between InPNWs and CH₄ to be physisorption.

7.3.3.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

FTIR spectra of CO, InPNWs and CH₄ are shown in Fig 7.21. The spectra were comparable to those reported in the literature in regard to the peak positions [25, 27-28]. The CO asymmetric and symmetric stretches showed a peak at 2143 cm⁻¹ [25]. Moreover, CH₄ showed a typical C-H bend and stretch at 1300 cm⁻¹ and 3000 cm⁻¹, respectively [27]. A weak stretch at a wavenumber of 2940 cm⁻¹ was ascribed to InP [28].

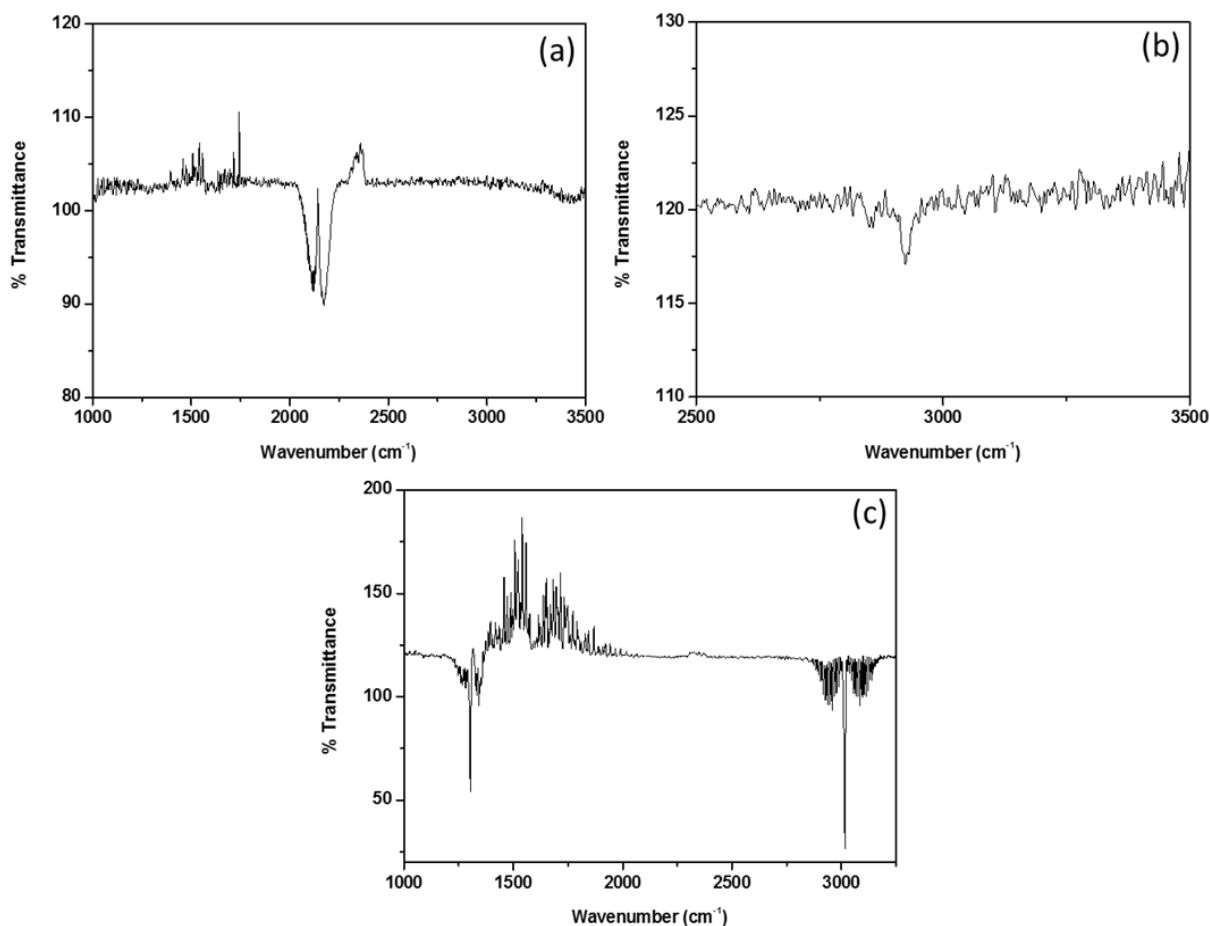


Figure 7.21: Infrared spectra of (a) carbon monoxide, (b) indium phosphide and (c) methane.

7.3.3.2.1 Interaction of InPNWs with CH₄

DRIFTS spectra of CH₄ over InPNWs recorded at different time intervals are shown in Fig 7.22. The spectra recorded after 30 minutes showed that CH₄ gas was completely purged out of the system suggesting weak or no interaction of methane to InPNWs. TPD results of InPNWs and CH₄ suggested adsorption which was limited to lower temperatures (-45°C to -15 °C) and enthalpy of desorption was calculated to be less than 50 kJ/mol suggesting physisorption. Physisorption is characterised by weak Van der Waals forces that could easily be broken during purging leading to CH₄ being removed from the surface of InPNWs [29].

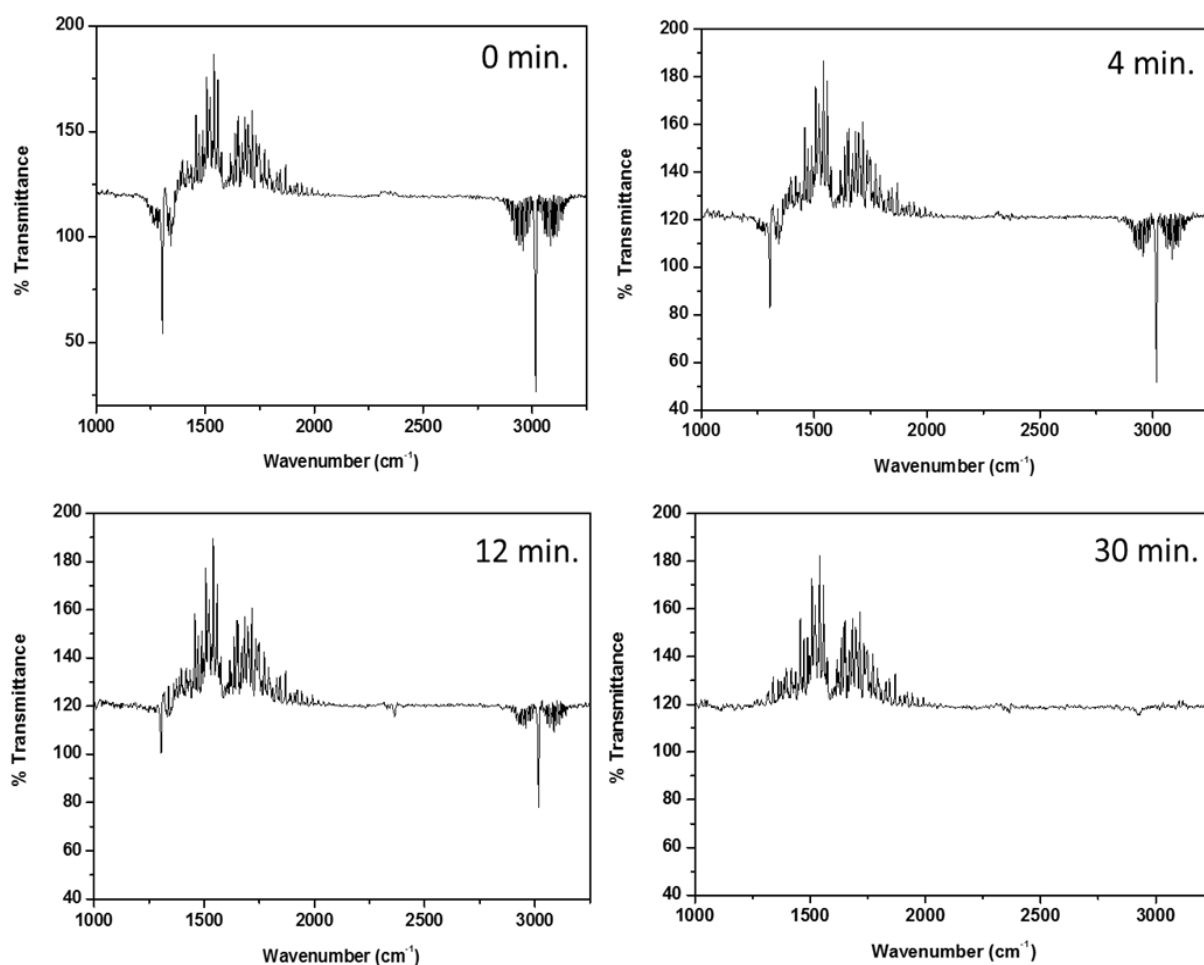


Figure 7.22: FTIR spectra of CH₄ molecule showing both stretching and bending peaks at 3100 cm⁻¹ and 1500 cm⁻¹, respectively as the purging time was increased up to 30 minutes.

7.3.3.2.2 Interaction of InPNWs with CO

DRIFTS results of InPNWs and CO gas recorded at different time intervals are shown in Fig. 7.23. The room temperature results showed that there was no interaction between the InPNWs and CO molecules. When the temperature was raised to 250°C and the same experiment was conducted, at 0 minutes purging time two peaks were observed. The primary peak at 2143 cm⁻¹ is characteristic of gaseous CO [30] shown in Fig. 7.23 (0 minutes). The secondary peak at 1920 cm⁻¹ was due to CO stretch that was weakened due to the formation of the new bond(s) with the InPNWs binding sites on the surface.

A single bond with a longer bond length between two atoms is weaker than multiple bonds with shorter bond length. Single or double bonds are recorded at lower wavenumber when

compared to triple bonds. As shown in Fig. 7.23, there is a peak that appeared at a wavenumber of 1920 cm^{-1} . The peak at a wavenumber of 2143 cm^{-1} which was ascribed to gaseous CO disappeared as the purging time was increased to 30 minutes. Crucial to note is that the peak ascribed to CO adsorbed onto InPNWs (1900 cm^{-1}) remained intact, after purging with helium gas for 30 minutes. This indicated a strong molecular adsorption of CO to the InPNW's binding sites.

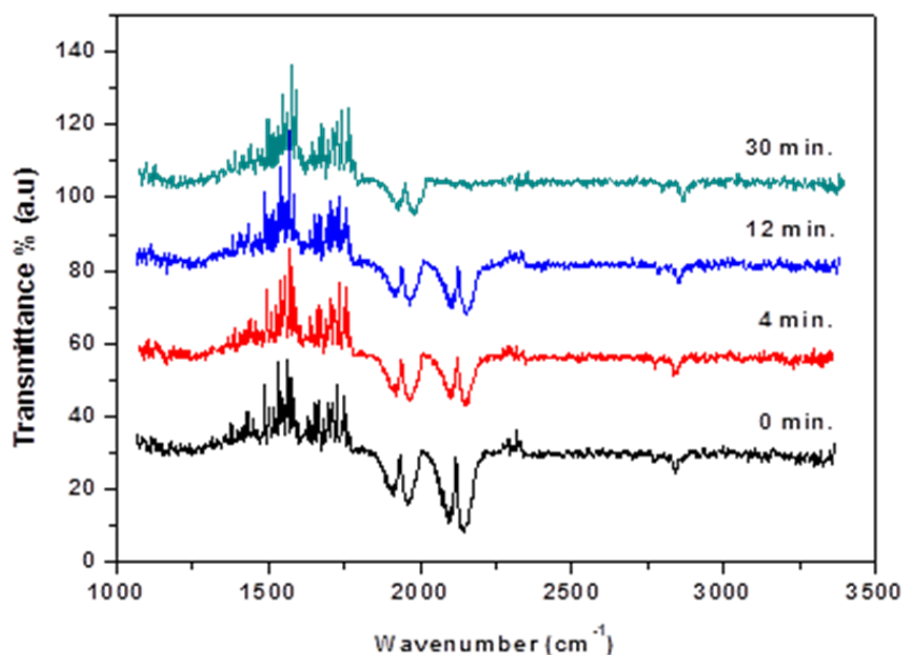


Figure 7.23: FTIR spectra of CO molecule showing stretching and bending peaks at time intervals of 0, 4, 12 and 30 minutes.

The most common binding modes of CO molecules to binding sites are linear, 2f bridged and 3f hollow bridged as shown in Fig. 7.24 [19, 30]. T. Baidya *et al* predicted the position of the CO vibrations when attached through linear to be between $2000\text{ cm}^{-1} - 2100\text{ cm}^{-1}$, 2f hollow bridged to be $1900 - 2000\text{ cm}^{-1}$ and 3f bridged to be $<1900\text{ cm}^{-1}$ [30-36]. The secondary CO peak was found to be at a wavenumber of 1920 cm^{-1} . Therefore, the secondary peak could be assigned to a carbonyl species chemisorbed through 2f hollow bridged bonded CO (Fig. 7.24 b) inserts showing a 3-dimensional configuration. The absence of peaks like OH suggests that the surface of the InPNWs is free from defects and impurities. This implies a direct interaction of the gas with the surface.

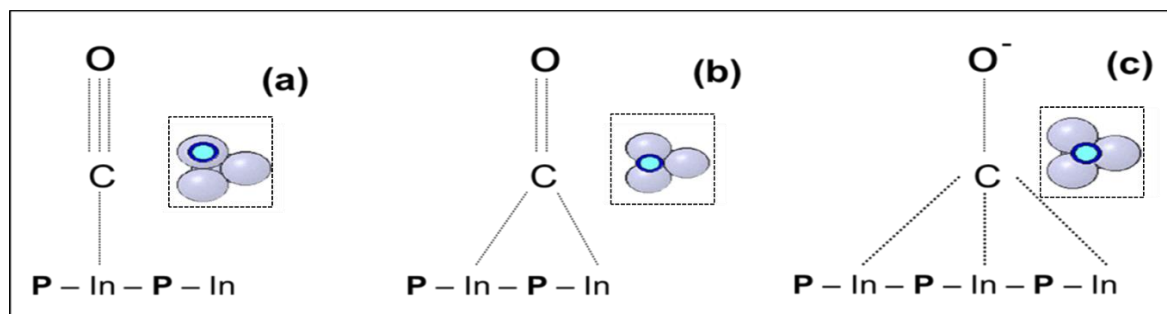


Figure 7.24: CO binding modes (a) linear/ terminal (b) 2f hollow bridged and (c) bridged 3f hollow.

7.3.3.3 Monte Carlo Simulation of CO and InPNWs Adsorption

Predictions through simulation of the interaction between InPNWs [111] cleaved surface and CO molecule are shown in Fig. 7.25 (a). The carbon atom from the CO molecule was found to interact directly with the phosphorus from the InPNWs and the oxygen atom with indium. The bridged configuration made this a 2f hollow bridged interaction as shown in Fig 7.25 (b). The interaction of InPNWs with CO holds promise for InPNW-based gas sensor.

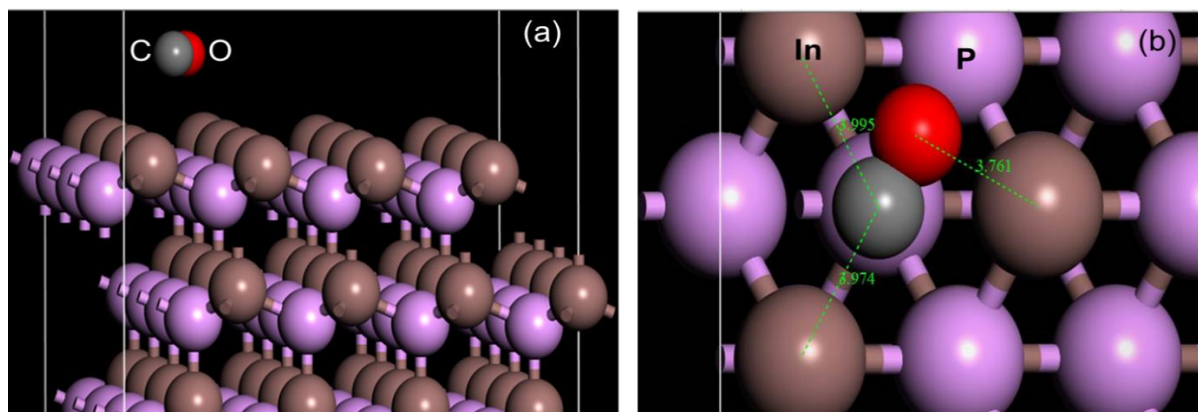


Figure 7.25: Monte Carlo simulation of interaction between InPNWs and CO molecules.

7.3.4 Indium Phosphide Nanowires based Gas Sensor

InPNWs were integrated into a multiple electrode device with the electrodes separated by a distance of 1 μm . The InPNWs were randomly interconnected to form a network necessary for electrical conduction. The InPNW integrated gas sensor device was exposed to analyte

gases such as CO and CH₄ separately at temperatures of 250°C and 300°C. These gases were chosen because they are noxious and are greenhouse gases. Additionally, H₂ and NO₂ were also tested and the results are discussed.

The electrical conductivity of the InPNWs was monitored both in the absence and presence of the analyte gases. The graphs showing a change in electrical conductivity in the presence and absence of analyte gases is shown in Fig 7.26. Analyte gas molecules adsorbed on the surface of InPNWs affected the electrical conductivity. The measured electrical conductivity of InPNWs was reduced when the analyte gas was adsorbed on the surface of the InPNWs. The reduction of electrical conductivity during gas adsorption is typical for p-type semiconductors when exposed to reducing gases such as CO and NO₂ [36]. The change in the electrical conductivity of InPNWs was found to be higher at elevated temperatures for CO and CH₄ as shown in Fig. 7.26 (a). It was observed that the response of InPNWs to CH₄ was significantly better than that of CO at 300°C. TPD and DRIFTS confirmed that CH₄ adsorbed to the InPNWs through physisorption. Contrarily, it has been reported by K. Raghavachari *et al* that hydrogen-containing gases break the In-In and In-P bonds to form In-H and P-H [37]. This accounts for a significant reduction in InPNW's electrical conductivity upon exposure to CH₄. On the other hand, it is possible that on the surface of the InPNWs grains, adsorbed oxygen molecules from the environment extract electrons from the conduction band and trap them on the surface in the form of ions. These ions then produce a band bending and an electron depleted region called the space-charge layer. The interaction of the gas with the space-charge remarkably increases the sensitivity of the sensor.

Gases such as CO and NO₂ have valence electrons which aid in the adsorption through chemical bond formation with the InPNWs. Adsorption of CO on InPNWs was determined to be chemisorption using TPD and DRIFTS.

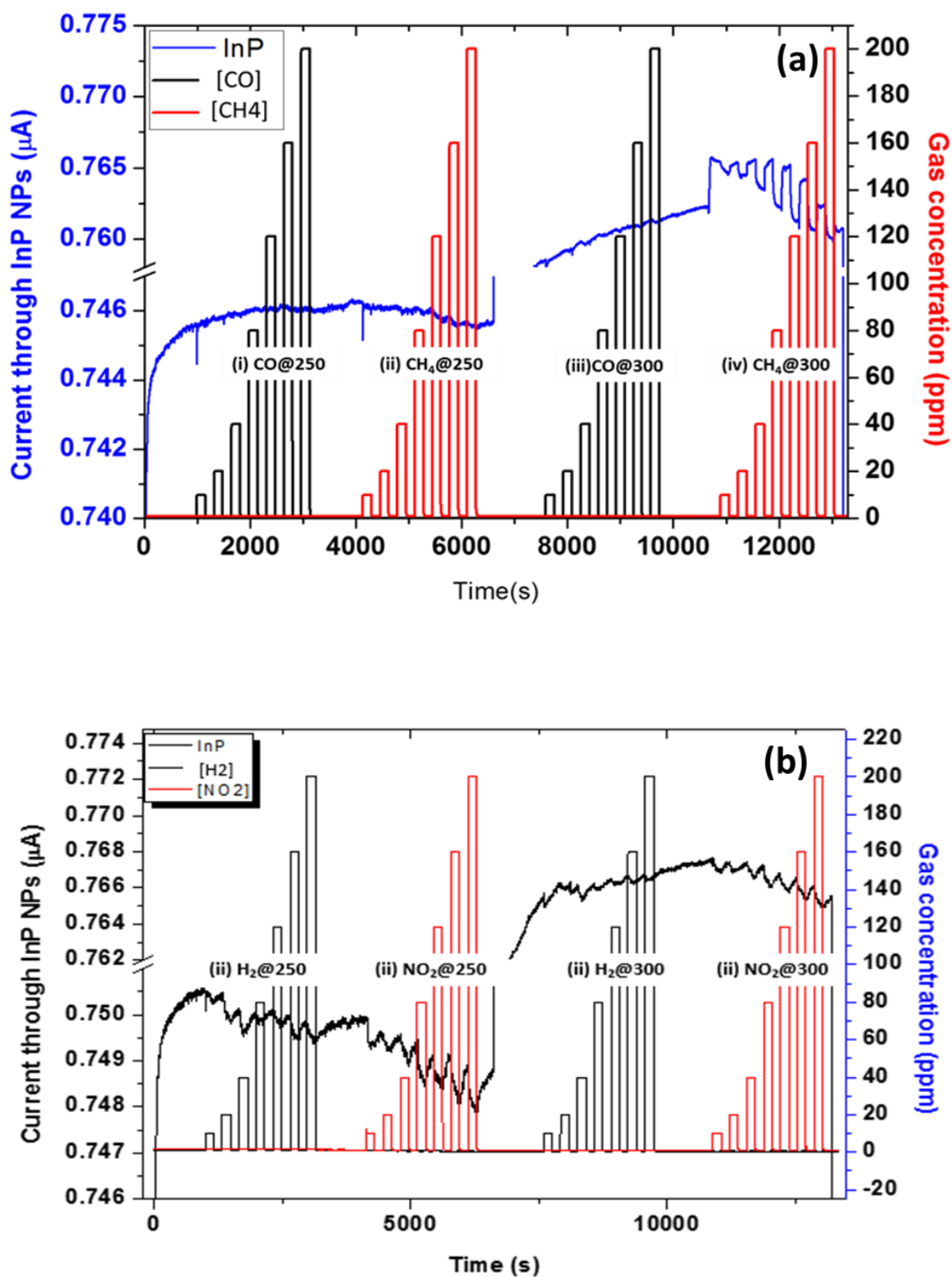


Figure 7.26: Electrical current changes of indium phosphide nanowires when exposed to different analyte gases such as (a) i. CO at 250°C, ii. CH₄ at 250°C, iii. CO at 300°C, and iv. CH₄ at 300°C and (b) i. H₂ at 250°C, ii. NO₂ at 250°C, iii. H₂ at 300°C, and iv. NO₂ at 300°C.

Response times were calculated by fitting an exponential decay curve to 160 ppm data using Equation 7.3 and are tabulated in Table 7.1.

$$y = A e\left(-\frac{x}{t1}\right) + y0 \dots\dots\dots \text{Equation 7.3}$$

CO response time was the quickest with a response time of 27s at 250°C of all the analyte gases. This quick response time for CO could be attributed to the bond formation between CO molecules and InPNWs. The bond formation has potential to decrease the electrical conductivity of InPNWs quicker producing a fast response since InP is a p-type semiconductor. InPNWs had the fastest response time for hydrogen gas at a temperature of 300°C, which could be attributed to a higher rate of forming new bonds like In-H and P-H compared to lower temperature as previously reported by Raghavachari *et al* [37].

Table 7.1: Indium phosphide nanowire’s response times for carbon monoxide, nitrogen oxide, hydrogen and methane gases.

Temperature (°C)	Response times (s)			
	CO	CH ₄	H ₂	NO ₂
250	27.19	80.68	175.81	48.36
300	55.48	69.38	52.95	108.20

InPNWs with relatively narrow size distribution provide relatively uniform sites for analyte gas to adsorb [29]. The gas adsorption on these sites is determined by the diameter of the nanowires and size distribution. Gas adsorption is largely affected by the size of the gas molecule, specific structure of the nanowires, total specific area of the nanowires, binding energy as well as availability and quantity of the binding sites. Nanowires, in general, possess large surface-to-volume ratios when compared to the conventional metal oxide thin films, a

phenomenon advantageous in gas sensing. The advantage of nanowires over metal oxides in gas sensing is ascribed to the high aspect ratio. Thus, these provide long semiconducting channels making them highly sensitive and efficient transducers of surface chemical processes into electrical signals [19].

The synthesis and purification of nanowires procedures were controlled to produce a single phase nanowires as seen from the XRD results. This was done to limit gas binding sites to InP phase and eliminate any ambiguity from any secondary phases. Raman also detected this single phase confirming high purity material. The narrow particle size distribution of the nanowires was also controlled for reproducibility of the adsorption of the analyte gas. All these factors contributed to the interaction of the analyte gas with the nanowires.

The thermal cleaning of nanowires before analysis by both TPD and DRIFTS was crucial in activating the surfaces of the nanowires. Heating InPNWs desorbed surface impurities like moisture, CO₂ and oxygen contribution from the environment. Thermal cleaning also caused surface reconstruction where indium atoms over-layers moved to the surface of the nanowires producing surface electron accumulation layer [38]. Surface electron accumulation layer is sensitive to gas adsorbed on the surface because it changes charge density of the nanowire. Change in charge density influences the material electron mobility subsequently affects gas sensing properties.

InPNWs have excellent electrical transport properties and are also known to have a high density of states. These properties are a direct result of non-passivated dangling bonds. Typically the surface states tend to act as surface charge traps making additional electronic states within the band gap causing the binding of Fermi level at the surface [39]. Generally, group III-V materials are known to have surface charge traps as a common problem. Often needing some sort of surface passivation to circumvent the problem. However, InP have a relatively good quality surface with relatively a high density of states [39].

InPNW's relatively small but uniform diameter and large surface area mean more atoms on their surface. This makes then energetically favourable for adsorption of other molecules. On the other hand the presence of an electron lone pair on the carbon atom means CO could form a covalent bond with the surface of InP.

B. Santhibhushan et al reported that the binding energies of In-V (V for any elements in group 5 of the periodic table) followed this trend $\text{InN} > \text{InP} > \text{InAs} > \text{InSb}$, showing that InN has the highest binding energy and the most stable contrary to InSb [40]. The InPNWs were chosen for the adsorption of gases since it is stable amongst the group In-V. Therefore, InPNWs were good candidate for the gas adsorption studies. The results revealed that CO gas was chemisorbed on the InPNWs which is not surprising since CO has a lone pair. The charge transfer is reported to be due to HOMO of CO which is σ -molecular orbital [40]. The InP-CO bond that was detected from the DRIFTS was due to a charge transfer from the CO gas through the lone pair. The CO attraction to the binding sites of InPNW was sufficient to break the intermolecular forces induced by dipole attraction between the CO gas molecules.

The CH_4 has no lone pair, therefore, adsorption could be achieved through new bond formation such as In-H with the surface of the InPNWs or through surface impurities that could facilitate surface reactivity. TPD and DRIFTS results of both CO and CH_4 were vital in predicting the nature of the interaction between the gases and the surface binding sites of InPNWs. Adsorption of analyte gases on the surface of the un-passivated surface of InPNWs caused a change in the electrical conductivity. InP is a p-type semiconductor meaning holes are the majority carriers and electrons are minority carriers, when a reducing gas such as CO donates electrons they cause a reduction in electrical current due to electron-hole pair recombination.

7.4 Conclusion

InPNWs with a zinc blende structure were successfully synthesized using indium metalloid and phosphorus through CVD. InPNWs were formed as a result of a direct reaction of indium and phosphorus and this occurred through the formation of rhombohedral In_3P intermediate phase. Indium metalloid acted as both growth material and catalyst, making the growth a SLS growth. The thermodynamically favourable zinc blend structure was formed via growth along the [111] plane. InPNWs contained stacking faults but their crystal planes did not change direction angle at the stacking fault boundary.

Single and multiple InPNW-based electronic devices were successfully fabricated. The resistivity of the InPNWs was calculated to be $50 \, \Omega \, \text{cm}$ from the I-V measurements.

InPNW's ability to conduct electricity shows that controlling polytypism during synthesis was successful in eliminating discontinuity of electron flow. The stacking faults of the InPNWs did not have adverse effects on the electrical properties of the InPNWs. These InPNWs could be further investigated for use in other devices like transistors and diodes.

TPD and DRIFTS results revealed that CO gas molecules were chemically adsorbed to the InPNWs but could be easily desorbed thermally between 220°C – 260°C (sorption temperature range). The TPD and DRIFTS also revealed that CH₄ molecules were physically adsorbed onto the InPNWs through weak van der Waals forces. The physical adsorption at $\approx$ 33°C of CH₄ is certainly not considered ideal for CH₄ gas sensors. The CO sorption temperature range was determined by TPD study and a 2f hollow bridged binding mode was through DRIFTS studies. InPNW's stability and low density of states render InPNWs ideal as CO gas detector in an electronic device. The sorption range (220–260°C) is the temperature at which InPNWs can be used as a CO gas sensor.

InPNWs could detect gases such as CO, CH₄, NO₂, and H₂ at high operational temperatures which was confirmed by TPD and DRIFTS results. InPNW has the quickest response time for CO compared to all the analyte gases tested at a temperature of 250°C. Response times of all the analyte gases were longer when the temperature was increased from 250°C to 300°C.

7.5 References

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Indium Arsenide Nanowires as Active Sensing Material in a Gas Sensors**8.1 Introduction**

Recently, indium arsenide (InAs) nanowires have attracted much attention in the semiconductor industry due to their unique properties and versatile applications in areas of electronic, photonic and sensing devices [1-2]. The ever-growing interest in InAs is in part driven by the tuneable small band gap (0.35 eV) making it widely used in diode lasers and infrared detectors [3-5]. Furthermore, InAs in nanowire form is known to have high electron mobility resulting from small electron effective mass [7-9]. In bulk form, InAs crystals typically exhibit a zinc blende structure whereas the use of synthesis methods such as chemical vapour deposition and epitaxy have been demonstrated to form nanowires with a wurtzite structure [10]. The coexistence of both the zinc-blende and wurtzite structures has been noted and reported elsewhere [10-11] and believed to emanate from the presence of structural defects and dislocations. The density of defects (i.e. stacking faults) tends to affect the crystal orientation thereby significantly reducing the electron mobility [11].

In the present work, InAs nanowires were grown using a catalyst-free chemical vapour deposition. The method was specifically chosen to reduce the stacking fault density in the crystal structure. The growth method utilized offers several advantages in terms of improved uniformity and high yield [12]. Although there are several methods to fabricate InAs nanowires such as laser-assisted catalytic growth, template-induced growth, oxide-assisted growth, etc. [13-15], the use of hydrogen gas as carrier gas along with reduced contact time compared to conventional approaches and controlled pressure proved indispensable in respect to material dimensions and defects [15].

A large part of this work has focused on the application of InAs in gas sensing of noxious gases such as H_2S and CO . Although metal oxide gas sensors are often preferred for operation at high temperatures [16], group III-V semiconductors have increasingly become more notable. InAs nanowires are particularly important for their high electron mobility, and intrinsic surface accumulation of electrons resulting from the presence of large density of

surface states [17-18]. As such the current work involves the study of adsorption and desorption of gas molecules on sensing materials as well as the contact interfaces between the analytes and sensing materials for enhanced sensitivity. The study is carried out using TPD and DRIFTS analyses.

8.2 Experimental Procedure

8.2.1 Synthesis of Indium Arsenide Nanowires using Chemical Vapour Deposition

A mass of 20 mg of arsenic powder was mixed with 20 mg of indium powder (50 wt. %) and ground using pestle and mortar to obtain a fine homogenous mixture. The mixture was loaded into the furnace and then purged with a mixture of argon (95%) and H₂ (5%) gases for 10 minutes at the flow-rate of 100 sccm. The flow-rate was reduced to 50 sccm and maintained for the duration of the experiment. The sample was heated isothermally at a heating rate of 20°C/minute to a temperature of either 600°C or 700°C and allowed residence time of 25 minutes.

8.3 Results and Discussion

8.3.1 Structural and Textural Properties

SEM images of arsenic particles and indium particles are shown in Fig. 8.1 (a) and (b) respectively. The arsenic powder was found to have particles with sizes between 1 µm and 200 µm. Arsenic particles exhibited a spherical but irregular shape and tended to form aggregates and clusters. Indium particles were found to be spherical with a monolithic structure with a particle size between 10 µm and 100 µm.

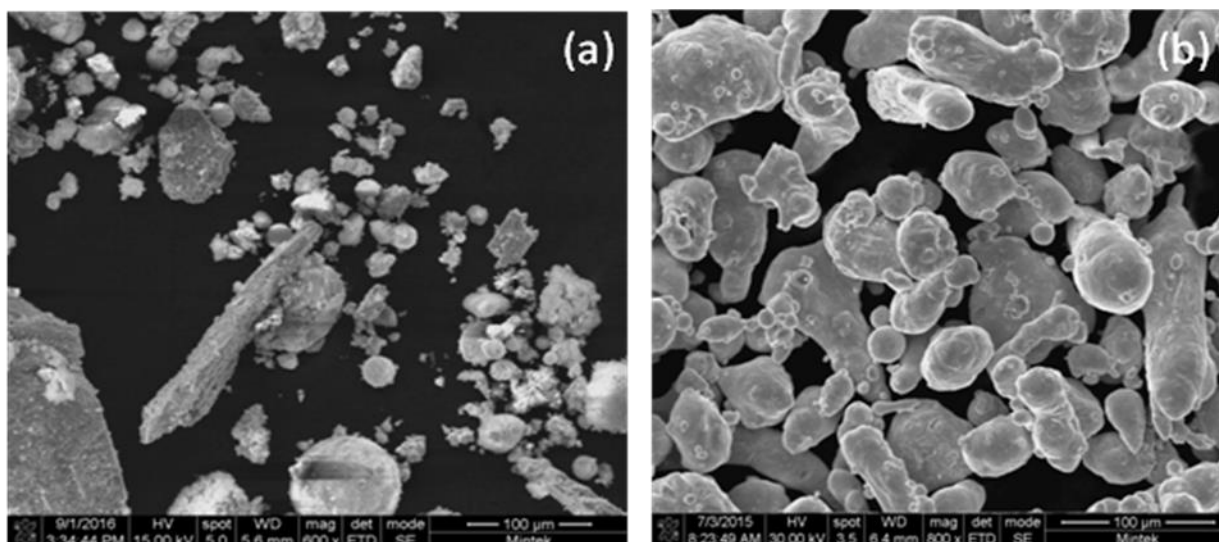


Figure 8.1: SEM images of (a) arsenic and (b) indium powders.

Fig 8.2 showed XRD patterns of the samples processed at 600°C and 700°C. The XRD pattern of the sample processed at 600°C (Fig 8.2 a) showed sharp and narrow peak at 2-theta angle of 48° [018] which could be indexed to arsenic. The sharp and narrow peaks observed at a 2-Theta angles of 60° [103], 66°[211] 69°[202] 74°[002] and 77°[101] were all indexed to indium (JCPDS, Card No. 4-784). These results revealed that at a relatively low temperature of 600°C, indium and arsenic powders did not react to form any product. However, the sample processed at 700°C (Fig 8.2 b) showed sharp and narrow peaks at 2-theta angles of 25° [111], 40° [220], 47° [311] which could all be indexed to cubic phase InAs (JCPDS, Card No. 4-784). The sharpness and narrowness nature of the peaks suggested that the InAs was crystalline. XRD pattern also showed that InAs was phase pure. The processing conditions for the sample prepared at 700°C are considered optimal and as such from this point further characterisation and analysis will be confined to this sample.

The formation InAs phase at 700°C meant that the reactant molecules have to absorb more thermal energy, thus high activation energy, in order to overcome the energy barrier [18]. The relatively high activation energy implies the formation of InAs is rather a slow process [18-19]. The reaction of arsenic and indium molecules took place only in a hydrogen environment.

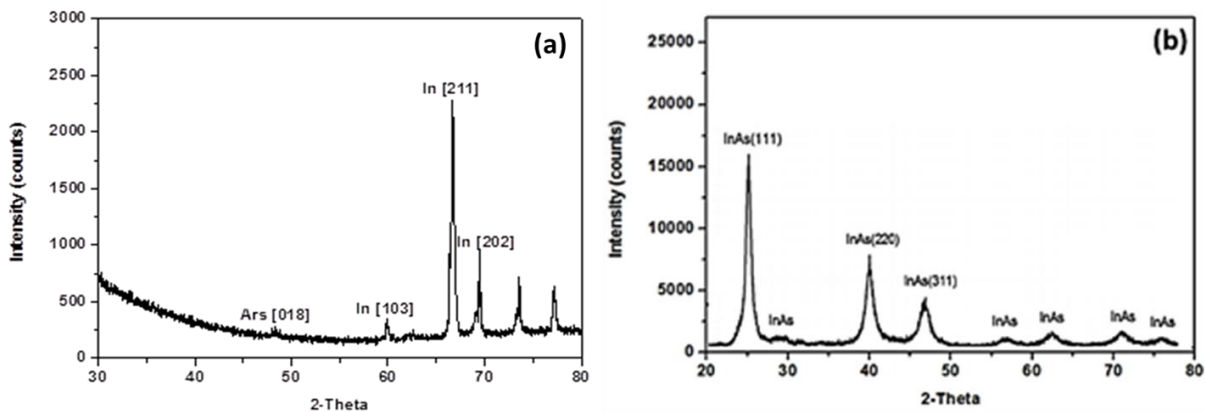


Figure 8.2: XRD patterns of the samples processed at (a) 600°C and (b) 700°C.

The SEM image of the sample prepared at 700°C (Fig. 8.3 a) revealed that the sample was composed of nanowire structures. These nanowires (InAsNWs) formed bundles, suggesting possible electrostatic attraction resulting from surface charge density [16-17]. EDX spectrum of InAsNWs is shown in Fig. 8.3 (b). Except for C peak from the sample holder, the presence of only indium and arsenic peaks indicates the formation of pure InAs nanowires. Elemental analysis carried out using EDX gave indium and arsenic ratio of 1.23, suggesting that the composition of the nanowires was comparable to the expected stoichiometry. Furthermore, the absence of unassigned peaks from XRD pattern is confirmatory of phase purity.

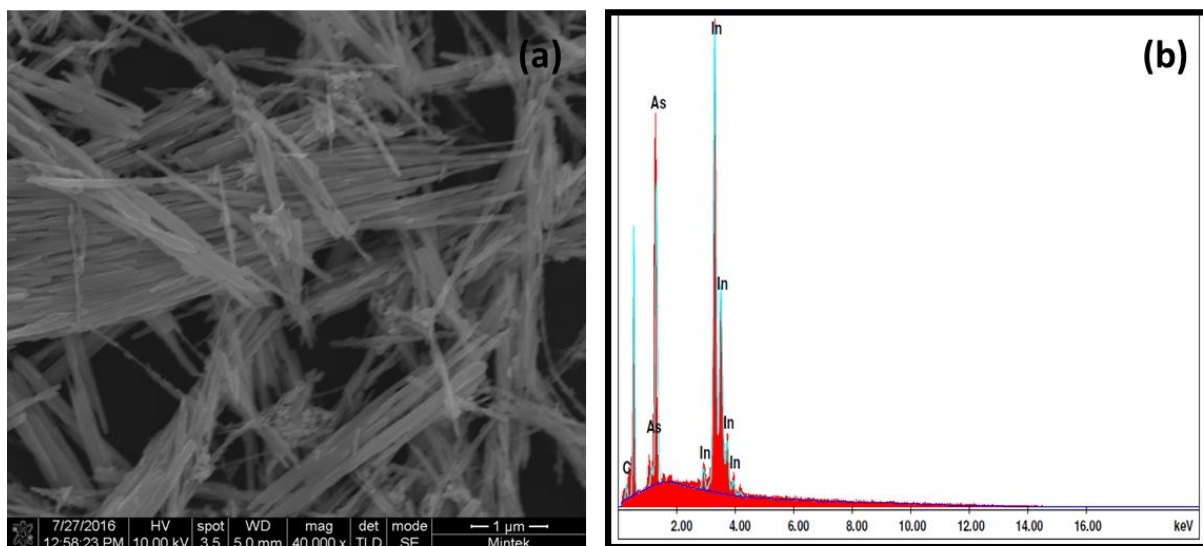


Figure 8.3: SEM image of (a) InAsNWs and their corresponding (b) EDX spectrum.

TEM image of InAsNWs shown in Fig. 8.4 (a) revealed that the nanowires were straight with an average diameter of 43 nm. The particle diameter is uniform along the nanowire and showed no tapering effects [10]. Controlling this dimension is particularly important in determining the degree of confinement and ultimately affecting the behaviour of charge carriers in quantum electronic devices. As such, it is fundamentally important to control the diameter of the nanowires individually because most device applications require a well-defined uniform diameter. TEM analysis confirmed the low defect density of the nanowires. Additionally, crystallographic defects such as stacking faults and polytypism tend to create non-radiative recombination centres which could adversely affect the performance of the device (electronic and optoelectronic devices) [11]. Particle size distribution histogram of InAsNWs in Fig 8.4 (b) showed narrow size distribution of 41 nm to 46 nm. The average length of the nanowires was found to be 500 nm. The formation of InAsNWs was autocatalysed by indium metal. Thus the process occurred via SLS mechanism - details explained in Chapter 7.

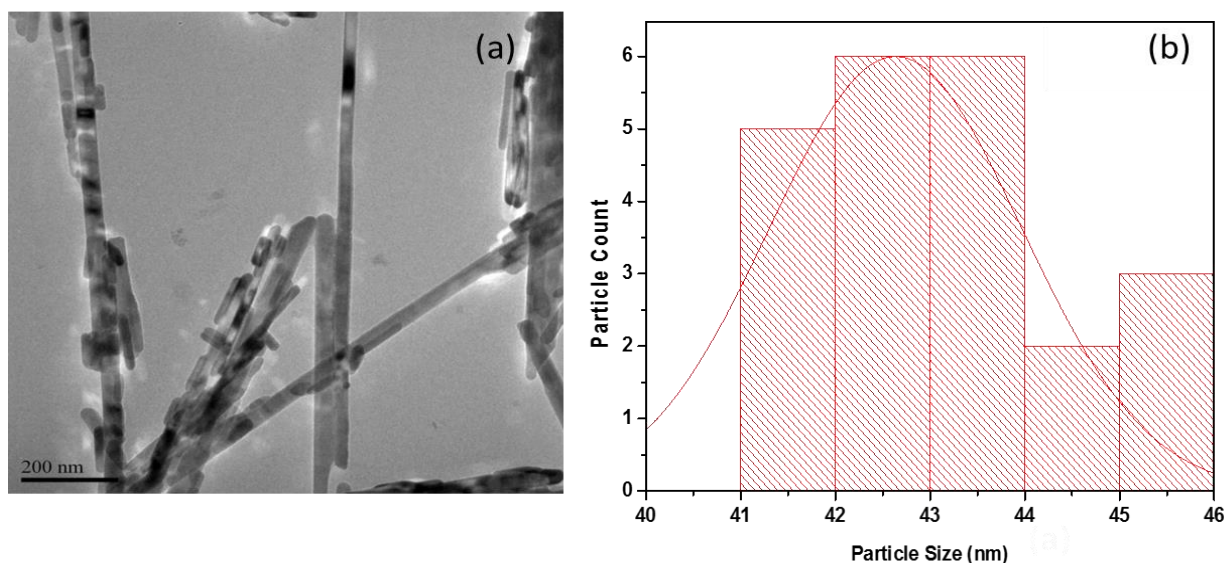


Figure 8.4: TEM image of (a) InAsNWs and (b) corresponding particle size distribution histogram.

The specific surface area and total pore volume of InAsNWs were measured to be $95 \text{ m}^2/\text{g}$ and $0.22 \text{ cm}^3/\text{g}$ respectively using Brunauer-Emmett-Teller (BET). The relatively large surface area of the nanowires is possibly due to the small size of nanowires as well as inter- and intra-particle porosity. The actual number of pores and pore diameter are expected to influence the specific surface area,

8.3.2 Indium Arsenide Gas Adsorption Studies: TPD and DRIFTS

8.3.2.1 Temperature Programmed Desorption (TPD)

Typical TPD profiles of CO and CH₄ gases on InAsNWs are shown in Fig 8.5. The temperature at which the M/Z signal (rate of desorption) was maximum ($T_{\max}$) was found to be 79°C for CO and -38°C for CH₄. The gas desorption range was found to be 70°C to 90°C for CO and -45°C to -30°C for CH₄. The monomodal distribution shown in the TPD profiles of CO and CH₄ gases on InAsNWs is characteristic of interaction occurring through the same set of binding sites. Enthalpy energy of desorption was calculated from extrapolated $T_{\max}$ values for each analyte gas using Redhead method (Equation 2) and was found to be 63 kJ/mol for CO and 31 kJ/mol for CH₄. The calculated enthalpy energies of desorption for CO and CH₄ suggest that the interactions were chemisorption and physisorption respectively.

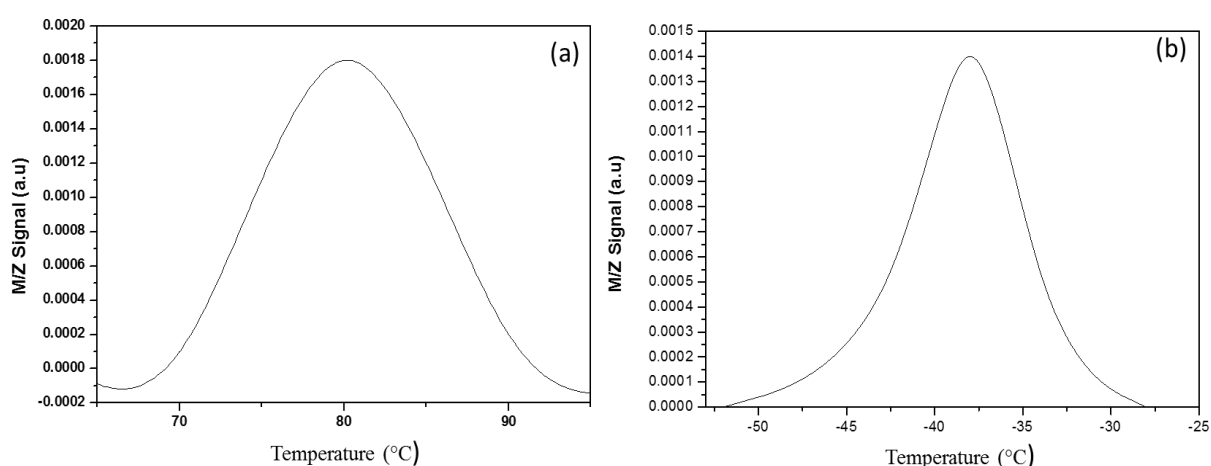


Figure 8.5: TPD profile of (a) CO and (b) CH₄ on the surface of InAsNWs.

8.3.2.2 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS results of CO and CH₄ did not show any peaks suggesting a typical weak interaction between the surface of InAsNWs and analyte gases. This was confirmatory of TPD results that revealed that physisorption interaction was due to weak van der Waals forces. Although the enthalpy energy for CO was found to correspond to chemisorption interaction, DRIFTS results revealed that CO was weakly bound to the surface of the nanowires, a phenomenon typical of physisorption interaction. This apparent contradiction could be explained in respect

to the fact that Redhead method is known to yield an error margin of ± 15 kJ/mol [20]. This suggests that even though the enthalpy energy of desorption of CO on InAsNWs was calculated to imply chemisorption interaction; it is now understood to correspond to a physisorption interaction. Increasing temperature of DRIFTS cell up to 300 °C showed no effects on the nature of the interaction.

8.3.3 Gas Sensing of Indium Arsenide Nanowires

InAsNWs were integrated into a multiple microelectrode device with a separation of 1 μm . The electrical conductivity of the InAsNWs was monitored both in the absence and presence of the analyte gases (CO and H₂S). The graphs showing a change in electrical conductivity in the presence and absence of analyte gases at different temperatures is shown in Fig. 8.6. The electrical conductivity of InAsNWs increased when the analyte gas was adsorbed onto the surface. The increase in electrical conductivity during gas adsorption is typical for n-type semiconductors when exposed to reducing gases such as CO and H₂S [21]. Therefore, electrons from analyte gases increased the electrical conductivity of InAsNWs since electrons are dominant charge carriers. InAsNWs were found to respond relatively better at higher temperatures than low temperatures as indicated by a significant increase in electrical conductivity at 300 °C when compared to 200 °C. This shows that the surface of nanowires required relatively high activation energy to interact with the analyte gases which is in agreement with DRIFTS results which showed no interaction at temperatures below 150 °C.

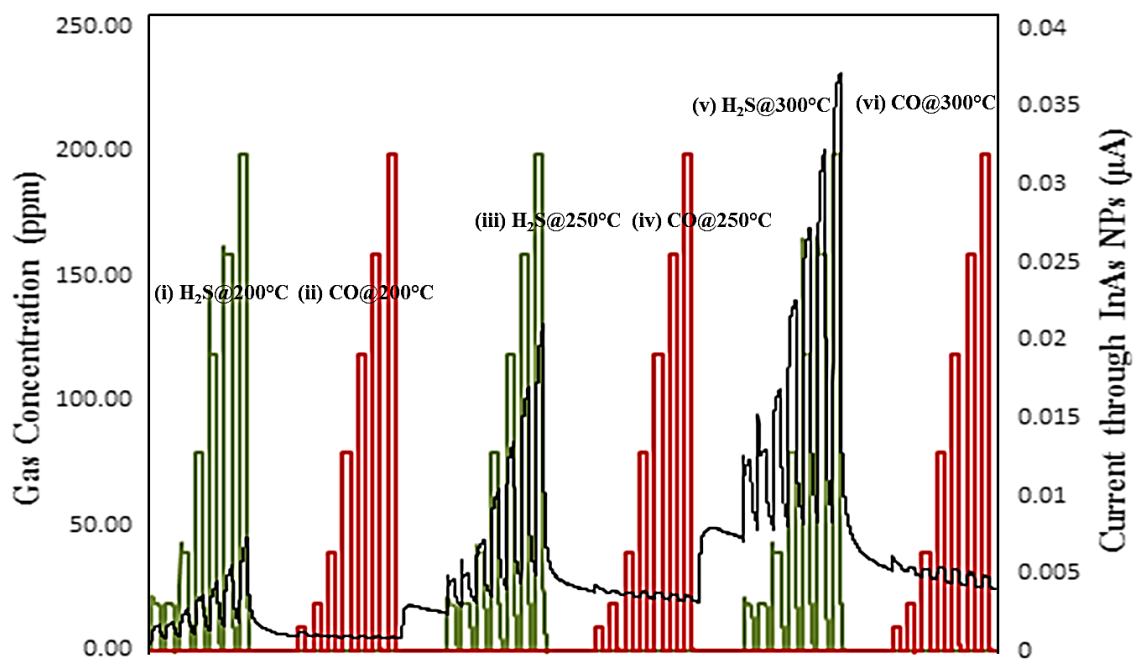


Figure 8.6: Electrical conductivity changes of InAsNWs when exposed to CO and H₂S gases at different temperatures.

The observed change in electrical conductivity of InAsNWs shown in Fig 8.6 was used to calculate response times at a gas concentration of 160 ppm. The response times for CO at 250°C and 300°C were 72s and 134s while those of H₂S were found to be 324s and 112s at 250°C and 300°C as shown in Table 8.1. The response times suggest that InAsNWs responded faster for CO when compared to H₂S at 250°C and 300°C. Response at 300°C was significantly slower, and this could be due to particle growth through Oswald ripening and possible collapse of the pore structure reducing the surface area of the material leading to poor trapping of gas molecules.

Table 8.1: Gas sensing response time of InAsNWs for CO and H₂S gases at 160 ppm.

Temperature (°C)	Response time (s)	
	CO	H ₂ S
250	72	324
300	134	212

8.3.4 Comparison of Gas Sensing Performance of InPNWs and InAsNWs

Nanowire-based sensor devices have demonstrated considerable promise for a new generation of chemical and biological detection. Indium arsenide and indium phosphide have high electron mobility and intrinsic surface accumulation layer of electrons and so as such hold properties beneficial for creating high-performance sensors that can be used in applications such as point-of-care testing for patients diagnosed with chronic diseases. Here, a comparison between InAs and InP nanowires is made in regard to material characteristics, sensor responses, and performance.

InAs nanowires are n-type semiconductors whereas InP nanowires are p-type semiconductors. InAs showed a decrease in electrical conductivity as the concentration of CO was increased. The change in conductivity is caused by adsorption of environmental oxygen gas molecule on the surface of the n-type nanowires. Furthermore, exposing InAs surface with oxygen ions adsorbate to CO leads to the electrons trapped by the oxygen ions adsorbate to return to the valence band. This essentially leads to a decrease in potential barrier height and subsequently increasing the electrical conductivity.

InAs recorded a slower response time of 72s for CO at 250°C when compared to that of InP, 27s for CO under the same conditions as shown in Table 8.2. The slower response is associated with the lower specific surface area (95 m²/g) and porosity (0.22 cm³/g) as reported for InAs. Comparison with InP shows that higher specific surface area and porosity

are directly related to adsorption rate of oxygen and response time. Although InAs nanowires have higher electron mobility ($40\,000\text{ cm}^2/\text{V}\cdot\text{s}$) than InP ($5600\text{ cm}^2/\text{V}\cdot\text{s}$) the response time appear to be dependent on the number of active sites on the surface. This clearly shows that the lower surface area leads to the reduced amount of oxygen molecules adsorbed on the surface.

There are different oxygen species that could be adsorbed on the surface of a semiconductor such as molecular (O_2^-) and atomic (O^- and O^{2-}) ions. The oxygen species depends on working temperature. Generally, below 150°C the molecular form dominates while above this temperature the atomic species are found [42]. The sorption range of InAsNWs was below 150°C (i.e. 70°C to 90°C). This means the oxygen species responsible for gas sensing were molecular ions and these are known to be loosely bound to the surfaces compared to atomic ions. This is the reason why a relatively lower enthalpy energy of desorption of 63 kJ/mol for InAsNWs was measured compared to 142 kJ/mol for InPNWs.

Table 8.2: Synthesis conditions, physical properties and response times of InPNWs and InAsNWs.

Property	InAsNWs	InPNWs
Specific surface area	$95\text{ m}^2/\text{g}$	$135\text{ m}^2/\text{g}$
Specific pore volume	$0.22\text{ cm}^3/\text{g}$	$0.31\text{ cm}^3/\text{g}$
Energy of desorption	63 kJ/mol (T: 70°C to 90°C)	142 kJ/mol (T: 215°C to 270°C)
Response time	72 s for CO at 250°C	27 s for CO at 250°C

8.4 Conclusion

InAsNWs with an average diameter of 43 nm were successfully synthesized using thermal CVD method, in a hydrogen environment. The InAsNWs were elementally and phase pure. TPD and DRIFTS results revealed that CO and CH₄ gas molecules were physically adsorbed onto InAsNWs and could be thermally desorbed. The temperature stability, surface area, and oxygen ion layer are all important to improve gas sensing capabilities of a material. Material with a large surface area and high porosity produce evenly distributed electron depleted sites that are important for gas sensing. Calculated response times of InAsNWs for CO were 72s and 324s and for H₂S they were 137s and 212s at 250°C and 300°C respectively. CO gas sensing response time of InAsNWs was found to be slower than that of InPNWs at 250°C.

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General Conclusions and Recommendations for Future Work

9.1 Conclusions

The common theme linking the chapters together was the synthesis of a metal-based catalyst. The chapters where new results were found are summarised as follows:

- (a) Controlled synthesis of gold nanoclusters for potential use as catalyst in the growth of semiconductor nanowires (**Chapter 4**).
- (b) Systematic control of size and morphology of gold nanoclusters for use as a catalyst in the growth of semiconductor nanowires (**Chapter 5**).
- (c) Gold catalysed growth of silicon nanowires for application in electronic devices (**Chapter 6**).
- (d) The use of auto-catalyst for controlled defects and lattice distortions of group III-V semiconductors for application in the fabrication of electronic devices (**Chapter 7 and 8**).

The formation of kinetically driven gold nanoclusters such as icosahedrons and decahedrons was achievable even though they are not thermodynamically stable. It was found that fast handling the gold seeds and limiting the gold source during gold nanoclusters growth had an effect in producing diverse shapes. Gold nanoclusters with decahedra particles were found to be the building blocks of icosahedra clusters which formed through the twinning mechanism.

The size and shape of gold nanoparticles were found to be affected by the choice of stabilising agent used. A relatively small molecule such as citrate was found to produce gold nanostructures with uniform particle size and narrow particle size distribution. The use of CTAB was found to produce various shapes such as spherical, triangular and irregular shaped gold nanostructures. The citrate concentration also had an influence on the size and size distribution of the gold nanoparticles.

The use of gold catalyst in the synthesis of SiNWs led to the formation of branched and interconnected nanowires using laser assisted catalytic growth method. Laser energy played a crucial role in controlling the resulting catalyst size which was found to be dependent on laser intensity. The size of the pristine gold metal nanoparticle was found to control the diameter of the resulting SiNWs.

InP and InAs nanowires were successfully synthesized using homogeneous catalysis through CVD. Both nanowires grew through the solid-liquid-solid growth mechanism with indium metal acting as both as the reactant material and a catalyst. The formation of InP and InAs nanowires to give optimum yield could only occur at 500-600°C for InPNWs and 600-700°C for InAsNWs. Below these temperature ranges the nanowires did not form and while at temperatures above the ranges the nanowires appeared disintegrated. The particle size, purity, crystal growth and porosity of InP and InAs nanowires were crucial in the gas adsorption performance. InPNWs were found to have quicker response time for CO gas than InAsNWs.

9.2 Future Work and Recommendations

The foregoing chapters have demonstrated the effectiveness of controlling the crystal growth and understanding the mechanism of formation of InP and InAs nanowires for improved performance of a gas sensor. However, in order to develop a functional sensing device it is expected that initiation of radically new technology that could potentially detect single entities or molecules could be achieved through unexplored collaborations between advanced multidisciplinary science and cutting-edge engineering. As such, more scientific exploration and exploitation of new technological possibilities, inspired by cutting edge science and new innovations through collaborations are imminent. Inspired by the results obtained in this work future work will include:

- Building a better understanding of the binding energy of the icosahedra and decahedra nanoclusters required to determine their temperature stability. Binding energy could be carried out using electron energy loss spectroscopy (EELS) to investigate the energy required to delaminate these nanostructures.
- Carrying out further studies on crystal growth of InP and InAs nanowires using laser assisted catalytic growth in order to;
 - (i) Investigate the effects of using a non-spherical gold nanoclusters on the shape of the resulting nanowires and
 - (ii) Exploring the effects it would have on the stacking faults and polytypism distortions.
- Making electrical measurements of InP and InAs nanowires at dilution temperatures in order to understand the effects of temperature on nanowire magnetism and electrical conductivity. These properties could add value to knowledge generation and could lead to new applications.
- Evaluation of gas sensing performance of indium phosphide and indium arsenide nanowires in the presence of other analyte gases and different humidity levels in-order to determine the selectivity and sensitivity of the nanowires – development of commercial sensor.

10.1 Appendix

10.1.1 Publications



Figure 10.1: Front page of the work published in journal of nanoscience and nanotechnology in 2016.



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7th International Symposium On Macro- and Supramolecular Architectures and Materials

The Effects of gold seeds stabilizing agent on gold nanostructures morphologies

Sanele Nyembe^{1,2}, Siyasanga Mpelane¹, Poslet Shumbula¹, Richard Harris¹, Nosipho Moloto², Lucky Sikhwivhilu^{1*}

¹*DST/Mintek Nanotechnology Innovation Centre, Advanced Materials Division, Mintek, Private Bag X3015, Randburg, Johannesburg 2125, South Africa*

²*Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, South Africa*

Abstract

The synthesis of gold (Au) nanostructures was successfully achieved through a three-step heterogeneous nucleation process. Two different types of Au seeds were prepared using citrate and cetyltrimethylammonium (CTAB) as stabilisers. Citrate and CTAB stabilized seeds were used to grow Au nanostructures separately. The CTAB stabilized seeds produced larger particles, of various shapes, with an average particle size >120nm with a wide size distribution (50–200 nm). The triangular Au nanostructures present in the mixture had a 3 dimensional morphology (i.e. pyramid shape) as confirmed by Atomic Force Microscopy (AFM). The citrate stabilized seeds were monodisperse and yielded well dispersed Au nanostructures with uniform morphology. These seeds had an average particle size of 50 nm with a narrow particle size distribution (45 – 55 nm).

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Keywords: Gold nanostructures, Morphology, Stabilizing agent, Gold seeds, Dispersity

Figure 10.2: Front page of the work published in materials today proceedings in 2015.