SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF INDIUM AND GALLIUM BASED NANOWIRES

By

ASMA AMIRA BINTI BADROL HISHAM

Supervisor: Prof. Dr. Ir. Cheong Kuan Yew

Dissertation submitted in partial fulfillment
of the requirement for the degree of Bachelor of Engineering with Honours
(Materials Engineering)

Universiti Sains Malaysia

JUNE 2017

DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Synthesis and Characterization of Indium and Gallium Based Nanowires**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title for any other examining body or University.

Name of Student : Asma Amira Binti Badrol Hisham Signature:

Date : 21 June 2017

Witness by

Supervisor : Prof. Dr. Ir. Cheong Kuan Yew Signature:

Date : 21 June 2017

ACKNOWLEDGEMENTS

First of all, I would like to thank the Almighty Allah for the strength and patience for me to complete this final year project and this report. I would like to gratefully and sincerely thank my supervisor, Prof. Dr. Ir. Cheong Kuan Yew for giving me the necessary advices and guidance throughout the experimental and thesis works until the end of my projects completion. I choose this moment to put on record my sincerest gratitude for all his contribution with great pleasure.

I would like to also wish to place my words of gratitude to Prof. Cheong's research team: Lim Zhe Xi, Asiah Noordin and Myo Myo for all the assistance and guidance provided to me throughout the entire project. Without their help and guidance, this project would not be able to complete within the time constraint.

Completing this work would have been all more difficult if not for the guidance and help from technical staffs of School of Materials and Mineral Resources Engineering. I will always be indebted to them, especially to Encik Azam in Electronics Lab and Encik Sayuti at the new lab building of School of Materials and Mineral Resources Engineering where the work of this thesis was mainly done.

I will strive to use gained skills and knowledge gathered throughout this 4 years studies in Universiti Sains Malaysia in the best possible way. I really appreciate the helps provides by School of Materials and Mineral Resources Engineering in terms of facilities and lab equipment for me to complete this project.

I would like to thank all my friends for their kindness and support during my studies. Finally, I would like to place my deepest thank to my family for their endless support, encouragement and financial support throughout my entire life.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

FESEM	Field Emission Scanning Electron Microscope
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscope
XRD	X-ray Diffraction
MBE	Molecular Beam Epitaxy
HVPE	Hydride Vapor Phase Epitaxy
Et al	and others
ICDD	International Center for Diffraction Data
JCPDS	Joint Committee on Powder Diffraction Standards

LIST OF SYMBOLS

In	Indium
Ga	Gallium
Au	Gold
ZnO	Zinc Oxide
In_2O_3	Indium Oxide
InGaN	Indium Gallium Nitride
InN	Indium Nitride
GaN	Gallium Nitride
HCl	Hydrochloric acid
InCl	Indium Chloride
N_2	Nitrogen gas
NH_3	Ammonia gas
~	around
°C	Degree Celsius
mg	milligram
nm	nanometer
%	percent
min	minutes
s	second

SINTESIS DAN PENCIRIAN WAYAR NANO BERASASKAN INDIUM DAN GALIUM

ABSTRAK

Dalam kajian ini, proses pembentukan wayar nano berasaskan indium, In dan gallium, Ga dikaji menggunakan proses wap kimia pemendapan. Bahan asas yang digunakan dalam kajian ini adalah logam indium, logam galium, gas ammonia dan emas sebagai pemangkin untuk pertumbuhan wayar nano di atas permukaan substrat nilam. Sampel yang telah disintesis dicirikan menggunakan Mikroskop Pengimbas Elektron (SEM), Spektroskopi Serakan Sinar-X, Mikroskop Transmisi Elektron (TEM), Belauan Sinar-X (XRD) dan Spektroskopi Raman. Parameter seperti suhu pertumbuhan (600°C, 700°C, 800°C dan 850°C), masa pertumbuhan (30 minit, 50 minit, 70 minit dan 90 minit), masa pemendapan lapisan nipis emas (1 saat, 2 saat and 3 saat), perbezaan antara bentuk emas pemangkin (zarah emas nano dan lapisan nipis emas) dan perbezaan nisbah In kepada Ga (30:70, 40:60, 50:50, 60:40 and 70:30), kesemuanya mempunyai kesan terhadap morfologi dan struktur wayar nano. Didapati bahawa suhu dan masa yang sesuai untuk pertumbuhan wayar nano adalah pada suhu 700°C selama 30 minit. Dengan 3 saat pemendapan emas, wayar nano yang terbentuk mempunyai tip bulat dan bentuk heliks yang bergulung sekitar paksi dengan pengagihan pertumbuhan yang bagus di atas permukaan substrat. Didapati nisbah In kepada Ga yang berbeza menyebabkan kesan terhadap panjang wayar nano yang terbentuk. Sampel yang disintesis dengan jumlah In yang lebih tinggi menghasilkan wayar nano yang lebih panjang dan sampel yang disintesis dengan jumlah Ga yang lebih tinggi menghasilkan wayar nano yang lebih pendek.

SYNTHESIS AND CHARACTERIZATION OF In- AND Ga- BASED NANOWIRES

ABSTRACT

In this work, formation of In- and Ga- based nanowires was studied using chemical vapor deposition (CVD) method. The starting materials were In, Ga and ammonia gas (NH_3) with gold as catalyst for the growth of nanowire on sapphire substrates. The samples were characterized by scanning electron microscopy equipped with energy dispersive X-ray spectroscopy, transmission electron microscopy, X-ray diffractometer and Raman Spectroscopy. Influence of growth parameters involved in CVD growth nanowires on morphology and structural of In- and Ga- based nanowires is presented. Growth parameters such as growth temperature (600°C, 700°C, 800°C and 850°C), growth time (30 mins, 50 mins, 70 mins and 90 mins), deposition time of gold thin film (1 second, 2 seconds and 3 seconds), different gold structure coating (gold nanoparticles and gold thin films) and ratio of metal sources (30:70, 40:60, 50:50, 60:40 and 70:30), In to Ga effected the structural and morphological of the formed nanowires. It is found that suitable temperature and time to grow the nanowires was at 700°C for 30 minutes. With 3 seconds deposited gold thin film, the formed nanowires appeared to have a rounded tip and helical structure of nanowire coils around an axis with a good distribution growth on the substrate surface. It is also found that different amount of In and Ga have an effect on the length of the formed nanowires. Samples synthesized with a higher amount of In formed a longer nanowires and sample synthesized with a higher amount of Ga formed a shorter nanowires.

CHAPTER 1

INTRODUCTION

1.1 Background

Recently, nanomaterials have garnered the interest of the world due to possessing unique properties applicable in the evolved technology while in small size. Nanotechnology is a branch of technology that utilized the use of nanomaterials. It is a term that explained on the science and engineering involved in the design, synthesis, characterization, and application of materials that are in nanoscale and are at least one dimensional.

The synthesis of In- and Ga- based nanowires are made possible by referring to the synthesis of InGaN nanowires. InGaN nanowires are a mixture of compound containing InN and GaN, which has drawn interest of researchers in recent years for its applications in light storage devices, due to high levels of quantum efficiency (Phillips, 2007). This is because each component has a slightly different band gap, InN have a band gap of 0.7 eV and GaN have a band gap of 3.4 eV, thus bridging a very wide emissions spectrum for InGaN alloy (Curry, 2015). The band gap of In- and Ga- based alloy nanowires is the one that makes it a good candidate for photoluminescence and light storage devices (Ye et al., 2007). One of the unique properties which are the most important is the large range of band gaps accessible with InGaN alloy, which made the synthesis by altering the compound ratio within the alloy to be possible (Curry, 2015).

Gallium nitride, GaN is one of the most research semiconductor materials due to its great properties for having high mobility and high electron drift saturation velocity, high thermal and mechanical stability and strong breakdown electrical field, while InN has large drift velocity at room temperature and low electron effective mass resulting in high mobility and high electron drift saturation velocity. Due to these prominent properties and potentials that can evolved more, possess by both semiconductor nanomaterials, various kinds of nanostructures such as nanowires, nanotubes, nanorods and nanosheets have been synthesized from both semiconductor either by individual stand or combined to form a compound alloy known as InGaN nanomaterials. The large lattice difference between InN and GaN due to fluctuations in chemical composition of InGaN has been recognized as likely the source of phase miscibility gap. Fluctuations in InGaN chemical compositions are likely to be the reason for the excellent in efficiency of these devices regardless of the high density of structural defects.

InGaN ternary alloys have become essential in nanotechnology due to their capability to contribute to tunable emission over the solar spectrum using a single crystalline structure by simply altering the alloy composition. The broad emission produced by these alloys has garnered interest especially in the development of white light emitting diodes, which can effectively minimize the mandatory lighting energy that illustrates the large fraction of the world energy consumption. (Ebaid *et al*., 2015). By reducing the dimensions of the InGaN ternary alloys to the nanoscale, especially in the nanowires form of which may improve the performance through reduced polarization fields and alloying strain, and increased in In composition (Hwa-Mok et al., 2004).

Many methods have been tried by researchers to synthesize In- and Ga- based nanowires, such as metal organic chemical vapor deposition and molecular beam epitaxy. Curry (2015) have reported on various methods on how to synthesis InGaN nanowires. One of the methods is by chemical vapor deposition (CVD) method. CVD method is a process used to deposit thin coatings on a substrate surface via chemical reactions of gaseous materials. Even though there are many other methods that have been employed to synthesize nanomaterials such as nanowires, these methods have their own restraints and disadvantages. CVD growth is the most practicable approach for growth of InGaN nanowires. Though the CVD growth of In- and Ga- based nanowires was reported, there has been no complete study about the growth parameter that influenced the morphology and structural of In- and Ga- based nanowires.

This work focused on the effect of growth parameters on the CVD growth nanowires. Growth parameters investigated were growth temperature, growth time, deposition time of gold thin film, different gold structure coating and ratio of metal sources, In to Ga. To this date, the GaN nanowires have been synthesized by various chemical vapor deposition methods in ammonia environment, which the gallium metal are used as the gallium source. The same method is employed in this work, with additional indium metal used as indium source to synthesize In- and Ga- based nanowires.

1.2 Problem Statement

Nanotechnology field has been explored and exploited by researchers lead to major advances in the synthesis and characterization department of nanomaterial. A variety of nanostructures material possessing appealing properties has garnered the interest of researchers to develop more techniques in order to synthesize more of these fascinating nanomaterials. These attempts have led to the accomplishment in the successful growth of alloy nanowires comprises of various elements including AuGa, Si, InN, InAs, GaN and GaAs, all of which have been implemented in electronic devices. Contrary to compound nanowires, oxide nanowires, such as ZnO, Ga_2O_3 and In_2O_3, are equally important.

Since the past few years, In- and Ga- based nanowires have been recognized to have good properties for application of luminescence and light storing devices causing an extensive amount of work done to investigate the properties of the nanowires. Curry (2015) have reported on the synthesis of InGaN nanowires using several fabrication methods include molecular beam epitaxy, vapor beam epitaxy, halide chemical vapor deposition, metal organic chemical vapor deposition, and vapor-liquid synthesis. Goodman et al. (2008) reported on the successful growth of InGaN nanowires using molecular beam epitaxy (MBE) method and the identification of the growth conditions to obtain good properties towards various applications. While there are many works have been done by other researchers on the application part of In- and Ga- based nanowires, it has been realized that not many works have been done to investigate the parameters involved to grow nanowires using chemical vapor deposition method. Ye *et al*. (2009) reported on the growth and field electron emission of InGaN nanowires properties formed by chemical vapor deposition tested using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron spectroscopy (TEM), X-ray diffraction (XRD) and room temperature PL with He-Cd laser (325nm) as the excitation source.

Formation of nanowires by chemical vapor deposition method is not new in the industry, while there are other methods to form nanowires. However, not many works have been done to investigate the growth of nanowires using CVD method due to uncontrolled growth condition that causes fluctuation in alloy composition. Therefore, the growth parameters involved using CVD methods are not thoroughly discovered. The formation of nanowires will be difficult if the growth parameters are not properly understood. The growth of nanowires depends on conditions like growth temperature, catalyst, growth time and metal sources. There are studies reported on the effect of growth parameters on the formed nanowires. Fluctuations in chemical compositions are likely to be the reason for the excellent in efficiency of these devices regardless of the high density of structural defects. Fluctuation in chemical compositions brings the large range of band gap which contributes to good optical properties of the alloy nanowires in the application of LED. Cai *et al*. (2007) reported that the growth parameters affect the morphology and structural of InGaN nanowires. Therefore, it is important to know the relationship between the growth parameters and the result of the synthesis of In- and Ga- based nanowires.

The work presented in this research uses a different approach on the growth parameters in synthesizing nanowires with a large range of band gap results from a large range of nanowires composition by chemical vapor deposition method. This method is a contamination free method of growth since no outside elements are introduced into the growth system. This research report includes experimental data and discussion on CVD growth effect on morphology and structural of In- and Ga- based nanowires grow on sapphire substrates. The finished samples were characterized by X-ray diffraction and Raman Spectroscopy to investigate the phase present on the nanowires. The samples also were characterized by FESEM and TEM for morphology studies.

1.3 Research Objectives

This project focuses on one component of nanomaterial system that is nanowires, specifically on InGaN nanowires. The research objectives are:

1. To synthesize In- and Ga- based nanowires on sapphire substrate using chemical vapor deposition (CVD) method.

2. To investigate the growth parameter of In- and Ga- based nanowires; growth temperature (600°C, 700°C, 800°C and 850°C), growth time (30 mins, 50 mins, 70 mins and 90 mins), deposition time of gold thin film (1 second, 2 seconds and 3 seconds), different gold structure coating (gold nanoparticles and gold thin films) and ratio of metal sources (30:70, 40:60, 50:50, 60:40 and 70:30), In to Ga.
3. To investigate the growth parameter effect on morphological and structural of In- and Ga- based nanowires.

1.4 Scope of Work

Nanowires compose of indium and gallium is of great interest in nanotechnologies due to the fluctuation in the alloy composition, which shows a range of observable properties in one material. This research, however, is focusing on the parameters involved to synthesize In- and Ga- based nanowires. Chemical vapor deposition (CVD) method was selected to promote the growth of In- and Ga- based nanowires on a substrate. Sapphire wafer was used as substrate for the nanowires formation instead of silicon wafer as silicon substrate has inadequate performance. The catalyst used was Au and the starting materials were Ga, In and NH_3.

The samples were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron spectroscopy (TEM), and X-ray diffraction (XRD) and Raman Spectroscopy. The influence of growth parameters on the morphology and structural of In- Ga- based nanowires were investigated.

1.5 Outline of Chapters

This research thesis is outlined in five chapters. Chapter one discusses the background studies, problem statements, research objectives and scopes of work done on the project. Chapter two explained about theory, concept and literature review behind the studies of chemical vapor deposition synthesizes In- and Ga- based nanowires. Scopes of work done are explained more in details related to the experimental procedure and characterization involved in Chapter three. Chapter four discusses all of the results gathered throughout this research. In Chapter five, conclusion and recommendation for future work are stated.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter is on the review of relevant literatures on: (1) Nanomaterials and nanowires, (2) Indium and Gallium based Nanowires, (3) In- and Ga- based technologies (4) Application of In- and Ga- based Nanowires and (5) formation of In- and Ga- based nanowires, specifically via Chemical Vapor Deposition method.

2.2 Nanomaterials and Nanowires

Nanotechnology is a subdivision under technology that involves the use of nanostructured materials. Nanostructured materials also known as nanomaterials are low-dimensional materials made up of building units in a submicron or nanoscale size at least in one direction plane and showcase size effects. Great control of nanometer scale structure properties can lead to development of new field to be evolved in new devices and technologies. The synthesis of nanomaterials must be closely controlled to control the results in nanomaterials sizes, shape and structure (Tiwari *et al*., 2012). Nanomaterials can be divided into three which are discrete nanomaterials, nanoscale device materials, and bulk nanomaterials.

Discrete nanomaterials are discontinuous materials that are within the range of 1–10 nm in size and are at least one dimensional. Discrete nanomaterials exist in the form of particles or fibers, which are zero-dimensional nanomaterials or one-dimensional nanomaterials, respectively. Figure 2.1 (a and b) shows the image of zero-dimensional nanomaterials and one-dimensional nanomaterials, respectively. Nanoscale device materials are elements contained within a device which are in a nanoscale size ranges. Nanoscale device materials are typically in the form of thin film which is a two-dimensional nanomaterials. Figure 2.1 (c) shows the image of nanosheets which is an example of two-dimensional nanomaterials. Bulk nanomaterials are nanomaterials conveniently available in bulk quantities, however still controlled at nanoscale size range. Bulk nanomaterials can be made up of discrete nanomaterials or nanoscale device materials which may combine to form a three-dimensional nanomaterial (Tiwari *et al*., 2012).

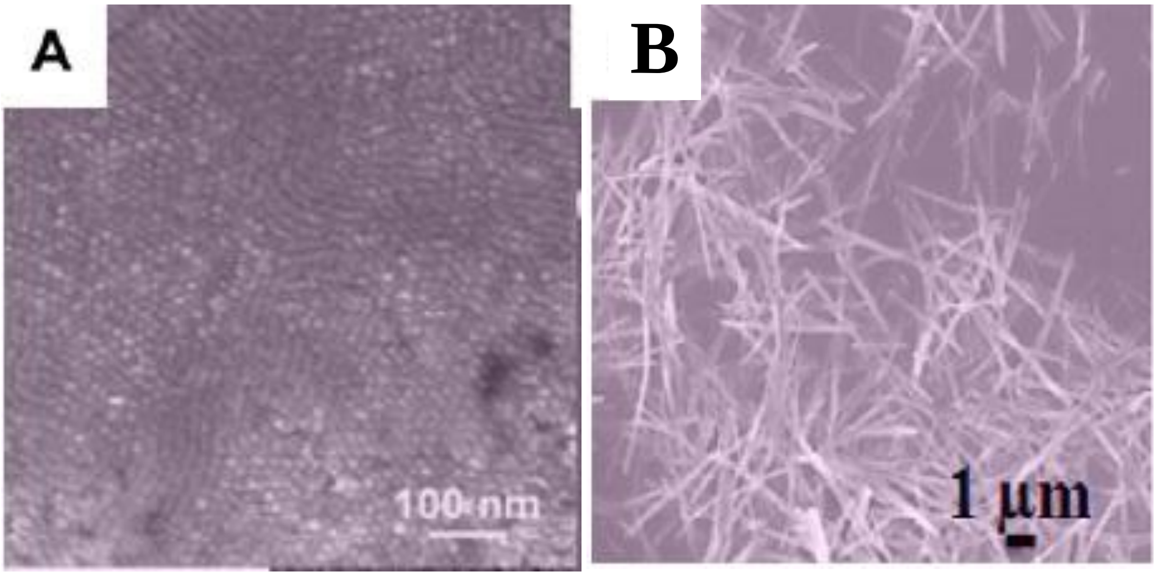

Figure 2.1: Several types of nanostructure: (a) Zero-dimensional nanomaterials in quantum dots form observed under SEM, (b) Image of nanowires observed under SEM, (c) Two-dimensional nanomaterials in nanosheets structure observed under TEM (Tiwari *et al*., 2012)

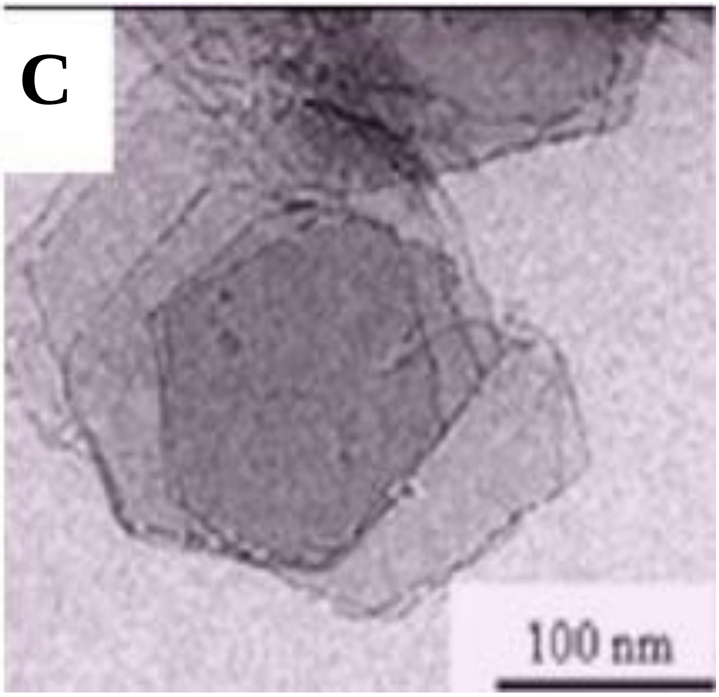

Figure 2.1: Continue

Nanowires are one of one-dimensional nanomaterials example with the diameter of nanometer range (10^{-9} m). The nanowires made up of highly ordered wires in nanoscale grown on a suitable substrate. Several methods have been developed to form nanowires with controlled growth parameters to synthesize desired results on size, composition and growth distribution. One of the methods is to synthesize nanowires is by chemical vapor deposition method. The growth parameters involved are: (i) the use of the anisotropic crystallographic structure of the substrate to make growth of nanowire easier, (ii) the introduction of a solid-liquid interface to reduce uniformity between the nanowires growth starting point, (iii) the use of blueprint to guide the nanowires growth, (iv) the use of exact control to change the growth pattern of the nanowires, (v) the use of limiting agents to manually control the growth rates of various nanowires plane and (vi) self-assembly of zero-dimensional nanomaterials within the nanowires (Müller *et al*., 2004).

2.3 Indium and Gallium based Nanowires

Nanowires based of indium and gallium are of great interest due to the wide range of composition ratio made possible by the flexible composition of the alloy, allowing a range of observable properties in one material.

The growth parameters involved in the formation of In- and Ga- based nanowires was studied by referring to the formation of InN and GaN nanowires. The catalyst used was gold and the starting materials were Ga, In and NH_3. InN has a band gap of 0.7 eV and GaN has a band gap of 3.4 eV. For $In_xGa_{1-x}N$ composition, if x varies from 0 to 1, the energy of optical emission will change from 3.4 eV to 0.7 eV, i.e., from ultraviolet (UV) to infrared (IR). (Cai *et al.*, 2009)

The band gap of combined InN and GaN alloy makes it a good candidate for luminescence and photodetection light storage devices. Past recent years, the researches done on materials that have good field electron emission properties have been developed more. Carbon-based materials, especially carbon nanotubes have been researched on and explore, however, the nanomaterials have a weak point that is it is easily oxidised, which makes them less significant if the parameters are not controlled (Xu *et al,* 2005). In- and Ga- based on InGaN nanowires, however, has a good resistance to oxidation. Even though research has been done on properties of ternary InGaN alloy nanomaterials, especially on photoluminescence properties, electron transport properties, phase separation and impurity doping properties, there have been no reports on the field electron emission properties of the nanowires (Kwon *et al*., 2005). If nanomaterials that have good field electron emission properties can be synthesized, the evolution of nanotechnologies, especially in optoelectronic devices and microelectronic devices can be achieved (Ye *et al.*, 2007).

2.4 In- and Ga- based Nanowires Technologies

The synthesis of nanowires made up of both indium and gallium has captured the interest of researcher in the past years for its significant in photo detection related devices, due to its properties of high levels of quantum productivity (Phillips *et al.,* 2007). A vast research has been done as early in 1998 to study the properties of InGaN and develop laser diodes made up of InGaN nanomaterials (Nakamura, 1998), and this research has been established more by the same researcher to develop blue-violet laser diodes which is still made effective in present-day in the form of modern compact disc technology (Nakamura *et al.*, 2000). In the current time, as the characteristic of InGaN has grown to be better, InGaN alloy in nanowires form has garnered the interest of researchers. This is due to escalate in research done on the established studies of nanowires, which imply that nanowires made up of InGaN alloy holds several unique properties convenient for the evolution of nanotechnologies in light storing devices (Law *et al.,* 2004). One of the unique properties which are the most important is the large range of band gaps accessible with InGaN alloy, which was synthesized by altering the compound ratio within the alloy (Curry, 2015).

InGaN nanowires were not synthesize by a same combination of the three individual elements, but rather a combination of InN and GaN alloy, giving a potential formulas of $In_xGa_{1-x}N$, each compound somewhat having a slightly dissimilar band gap, and thus bridging a very wide emissions spectrum (Curry, 2015).

Evolutions in the methods to synthesize the nanowires have naturally centered on producing the desired band gaps because any major employment of the materials band gap properties is important to produce full spectrum of InGaN stoichiometries. This is the major challenge faced by researchers of InGaN studies, due to notable difference in the lattice constants of both InN and GaN (O, 2001). In general, nanowires have shown to be astonishingly independent of the strain that usually coexist in alloys with large dissimilarity in lattice constant making the nanowires to be more appealing to those who seeks to thoroughly employ the capability of InGaN (Ertekin, 2005; Curry, 2015).

2.5 Application of In- and Ga- based Nanowires

In short period of time, the field of InGaN nanowires went from an unknown to a developed region in the nanotechnology application, with in depth characterization, understandable industrial applications, and a change in priority from accessing on how to synthesize the material, to comprehend on how to make it more efficiently and conveniently available. The adjustable band gap of InGaN alloy gives the material an immense amount of potential in the generation and conversion of light, which is usually comes in the form of nanowires. With a growing attention on the efficiency and solar energy, it is likely that request for these nanowires application will not weaken, however, there are likely for InGaN nanowires to have yet unknown uses for and their unique photoelectronic properties to have uncover more (Curry, 2015).

Due to these unique properties possess by the nanowires, these nanowires have garnered the interest for both traditional applications of the material as well as new purposes to be uncovered by researcher as the nanowires being developed. Nanowires evaluation shows that the evolution of InGaN nanostructures designated for established applications such as light emitting diodes photoluminescence and for materializes technologies, such as the photochemical conversion and reserve for solar energy (Yang, 2010). Prominent interest in InGaN as a solar energy converter through both photovoltaic cells and photochemical conversion has been the essence of vast research done in previous years due to band gap properties that enable the potential for conversion proficiencies to be greater than 50 % (McLaughlin, 2013).

2.6 Formation of In- and Ga- based Nanowires

Research on the formation of In- and Ga- based nanowires are based on the formation of InGaN nanowires. Many methods to synthesize InGaN nanowires have been researched on by researcher to form nanowires with desired properties. Among various methods used to grow InGaN nanowires are chemical vapor deposition and molecular beam epitaxy, MBE. Though the CVD growth of InGaN nanowires was reported, there has been no complete study about the parameter influence on the morphology of InGaN nanowires (Cai et al., 2009).

This section is centered on the developments of indium gallium nitride synthesis; contemplate on improvement in the fields of beam epitaxy, consists of vapor beam epitaxy and molecular beam epitaxy, and chemical vapor deposition, which can be divided into halide chemical vapor deposition, metal organic chemical vapor deposition, and vapor-liquid synthesis.

2.6.1 Hydride Vapor Phase Epitaxy, HVPE

Even though the work of Kim *et al.* (2004) are not on nanowire synthesis, in which Kim reported on synthesizing InGaN nanorods which the only different from nanowires is only by degrees, the notable work cannot be disregard, as it opens the faction to InGaN studies in the field. One of the methods to synthesize GaN nanowires is by using hydride vapor phase epitaxy method, as been done by Kim *et al.* (2004). The process is done in furnace containing gallium source and a sapphire wafer which served as the substrate for the nanorods to grow on. Inside the furnace, ammonia and nitrogen gas were pumped as metal chloride precursors of InGaN are synthesized by reacting high-temperature In and Ga with gaseous HCl in a N_2 carrier gas.

The InGaN nanorods produced from this synthesis showcase the materials great potential while showing the challenges of such synthesis. Scanning electron microscopy, SEM equipped with energy dispersive X-ray spectroscopy, EDX and transmission electron microscopy, TEM showed the presence of well-defined InGaN nanorods. However, when Kim *et al*. (2004) analyzed the nanorods composition, they reported that the nanorods composition to be rather limited, the composition was only in the range of x = 0.04- 0.20 for $In_xGa_{1-x}N$ due to the extended formation of the low-reactivity InCl, instead of $InCl_3$. As HCl gas pumped into the system, In metal source would react with HCl gas to formed the desired $InCl_3$, however, at sufficent partial pressures, by product of the reaction, H_2 could further respond to formed $InCl_3$, causing the indium to reduce to an inactive state.

In order to improve the synthesis of InGaN nanowires, Kim *et al.* (2004) reported additional work demonstrating a second method of synthesis, a branch of halide vapor phase epitaxy that is metal organic halide vapor pressure epitaxy. This synthesis method used another indium source, trimethyl-Indium, which is indium in the critical In^{3+} oxidation state crucial for InN formation. Targeting an emission of 470 nm, Kim el al. (2004) achieved in producing $In_xGa_{1-x}N$ with constant concentrations of x = 0.25, Figure 2.2 illustrates the results for the wavelengths available in SEM and TEM images.

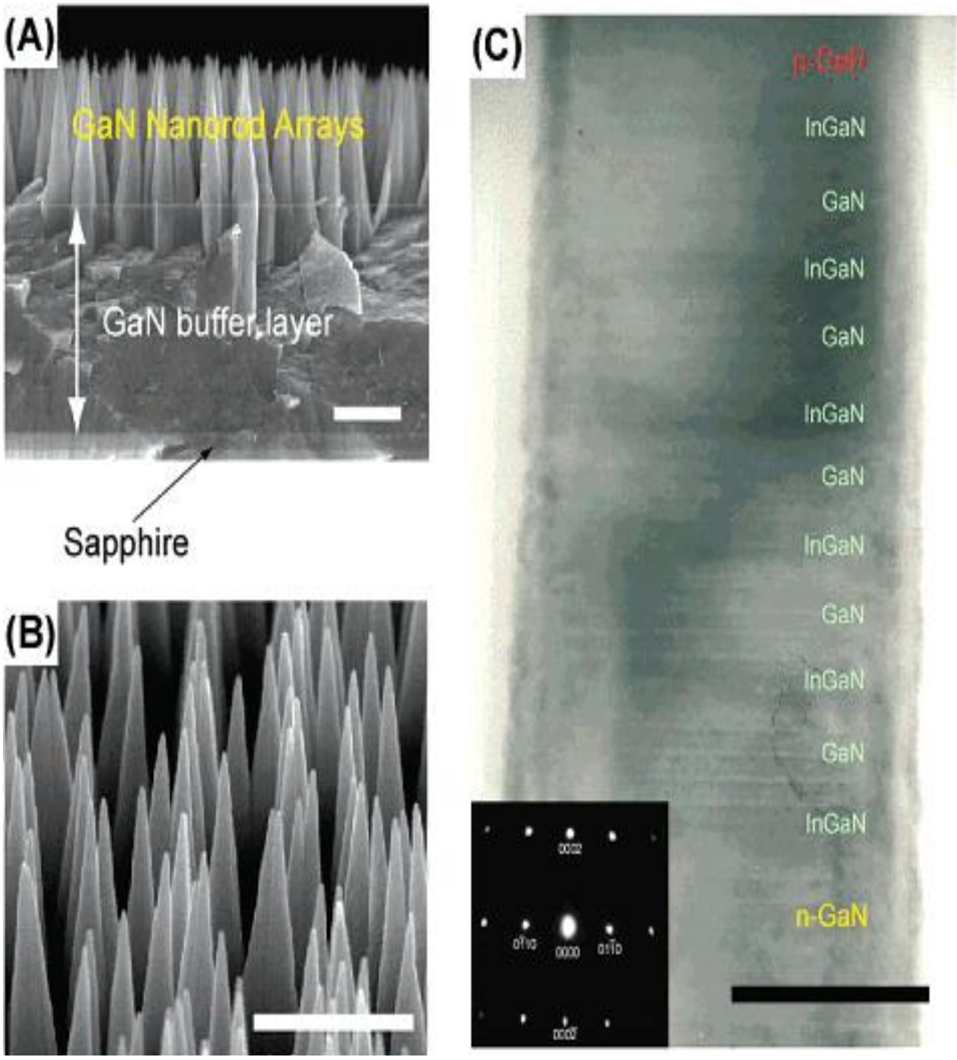

Figure 2.2: Scanning electron microscope (SEM) and transmission electron microscope (TEM) images (A) Cross-section-view SEM image of InGaN/GaN, (B) 30° tilt view of high-resolution SEM image of InGaN/GaN, (C) TEM image of $In_{0.25}Ga_{0.75}N$/GaN. The length and diameter of NR was about 1µm and 70 nm around the middle point of the nanorods. Scale bar is 30 nm. Inset shows the corresponding selective area electron diffraction (SAED) pattern (Kim et al., 2004).

2.6.2 Molecular Beam Epitaxy (MBE)

With a result in a definite ratio of $In_xGa_{1-x}N$ as desired, it is not a shocker that molecular beam epitaxy method has been explored as a mechanism of fabrication. Utilized in an ultra-high vacuum, the synthesis involves the reaction between high temperature molecules as the molecular beams on a crystalline surface (Cho *et al*., 1975).

Vajpeyi et al. (2009) utilized the use of nitrogen radio frequency as plasma source to deposit $In_xGa_{1-x}N$ directly onto a silicon substrate surface to synthesis nanopillars. It is revealed that by differing the substrate temperature, indium concentration coefficient x was inversely dependent to temperatures, however $In_xGa_{1-x}N$ nanopillars could not be deposited on the substrate below the temperature of 575°C. Other nanopillar properties like the density and diameter are linked with the substrate temperature showing that control of growth parameters are essential. However, while the temperature may have limited the possibility of full spectrum possess by the $In_xGa_{1-x}N$ nanopillars, Vajpeyi et al. (2009) managed to attain both spectrum range from 450 to 625 nm while still sustaining the limits on emission wavelength.

Figure 2.3 (a) shows the emissions wavelengths achieved by Vajpeyi et al. at room temperature wavelengths inset while maintaining the limits of emission wavelength, while Figure 2.3 (b) shows the relationship between substrate temperature and indium concentration (Curry, 2015).

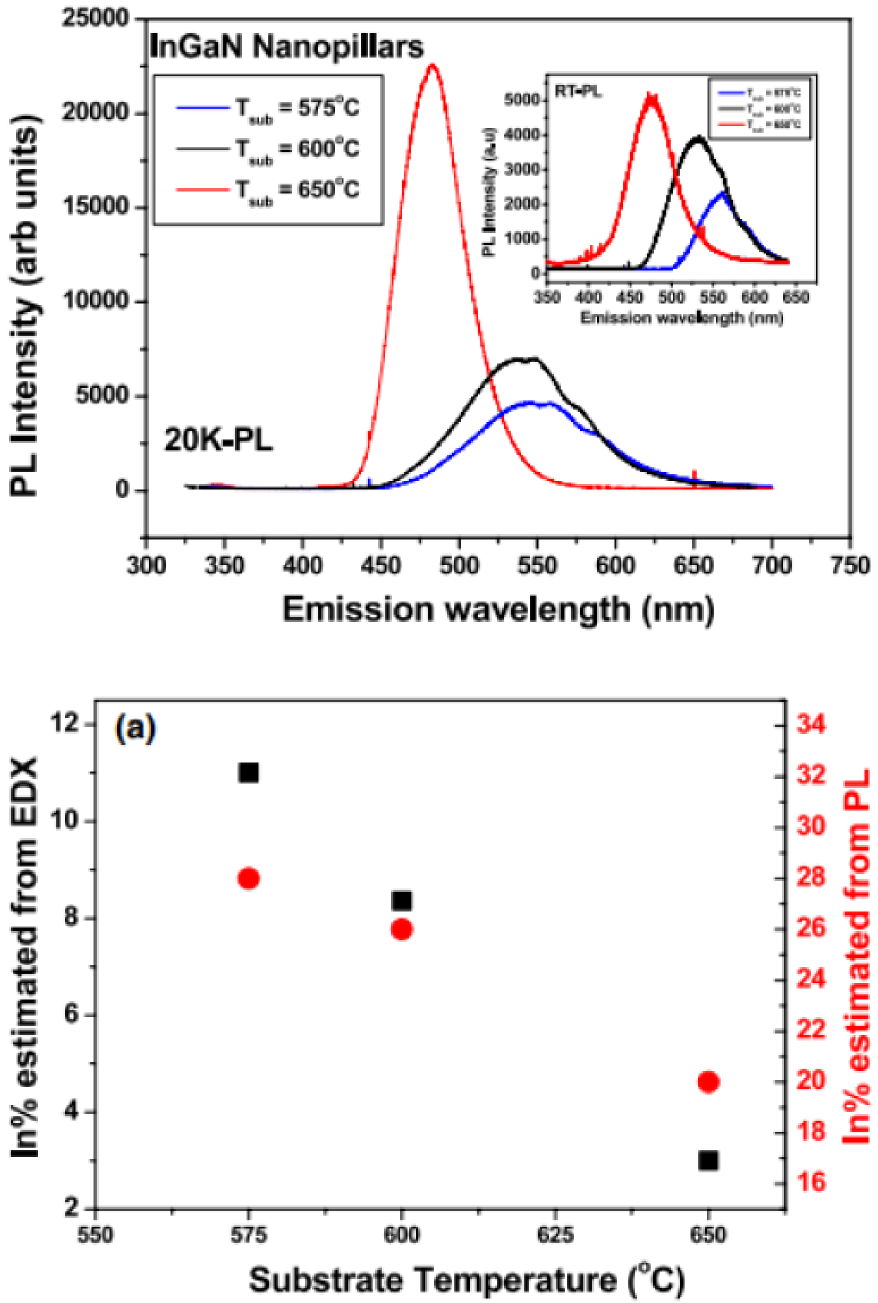

Figure 2.3: (a) the emissions wavelengths achieved by Vajpeyi et al, with their room temperature wavelengths inset. (b) The relationship between substrate temperature and indium concentration (Curry, 2015).

In past few years, Guo et al. (2010) strive to complete evaluation of MBE formed InGaN nanowires, using plasma-assisted MBE to alter the relative $In_xGa_{1-x}N$ fluctuation composition not by changing the substrate temperature, but by adjusting the

Influx occurred during synthesis of MBE grown nanowire. Through the work, Guo et al. (2010) succeed in not only synthesized nanowires composed of diverse amount of In which was not achieved in the previous MBE synthesis, but also succeed in forming nanowires in which the ratio of $In_xGa_{1-x}N$ change over the length of formed nanowire. The photoluminescence spectra showcased of InGaN synthesis which was not only has high precision for different ratios of $In_xGa_{1-x}N$, but also could control the broadness of emission to a degree in which it allows more or less focused wavelengths of light, and showing the true potential of MBE.

Figure 2.4 shows the photoluminescence spectra produced by the formed nanowire by Guo et al. (2010). The photoluminescence spectra showcased of InGaN synthesis in which the formed nanowires show high precision for different ratios of $In_xGa_{1-x}N$ along the length of nanowires.

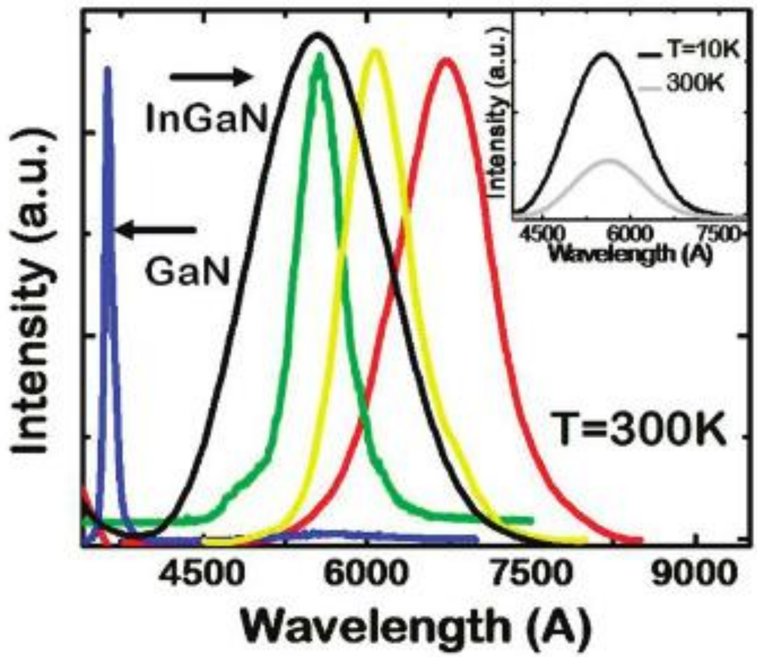

Figure 2.4: The photoluminescence spectra of the nanowire produced by Guo et al. (2010). The broad, black peak had varied concentrations of In throughout synthesis, while the colored peaks indicate relative purity. Inset is the temperature dependence of broad luminescence for the varied InGaN peak (Curry, 2015).

2.6.3 Halide Chemical Vapor Deposition

The most progress done in $In_xGa_{1-x}N$ synthesis, however, come in the field of halide chemical vapor deposition (HCVD), where Kuykendall et al. (2007) used an innovation in method to successfully synthesize and apprehend the entire range of $In_xGa_{1-x}N$ composition from x = 0 to x = 1. The synthesis designs were carefully done to bypass all the complication, such as unstable temperature, metal reaction, and lack of control from operator.

Figure 2.5 shows the optical characterization of the nanowires produced by Kuykendall, et al. (2007). Figure 2.5 (a) shows the color of CCD images, Figure 2.5 (b) shows the results of photoluminescence emission gathered from synthesized $In_xGa_{1-x}N$ nanowires with, x = 0 to x = 0:6. Figure 2.5 (d) shows the optical absorption spectra.

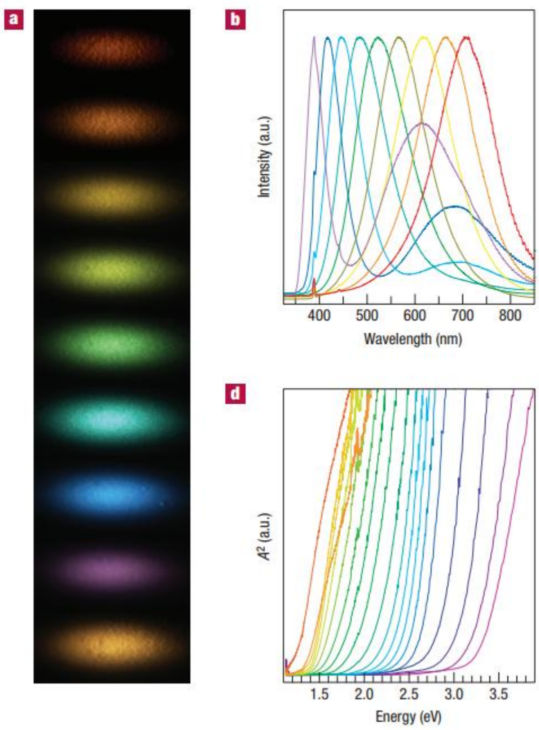

Figure 2.5: Optical characterization of the nanowires; (a) The color CCD images, (b) Photoluminescence emission from $In_xGa_{1-x}N$, x = 0 to x = 0:6, (d) Optical absorption spectra (Kuykendall et al.,2007).

These results permitted free vapor pressure control for both metal sources, keeping them in their oxidation state, I^{3+} and Ga^{3+}, at which when react to N_2 carrier gas allowed Kuykendall et al. (2007) to adjust the In ratio suitable to the composition of $In_xGa_{1-x}N$ nanowires grown on a sapphire substrate.

Regardless of the anticipated variance in the nanowire morphology, it did not cause any undesirable effect on synthesis of certain spectral configurations. Admittance to the full range of compositions fluctuation enabled full characterization to be done to access the structural properties such as lattice parameter, relative diameter, and shape, which directly linked them to the In fraction of full composition.

In an attempt to proceed on Kuykendall's work, Hahn et al. (2011) took to HCVD method and readjust more for practical used, Hahn et al. grows the nanowires on an Al_2O_3 substrate in the same furnace as Kuykendall et al. (2007) used, however, Hahn et al. (2011) refashion the method to produce homogenous arrays rather than a vast range of composition, Hahn et al. (2011) reported on an astonishingly quick growth of nanowires for about roughly 9 to 12 minutes. The formed nanowire arrays produced provide a chance to not only regulate a large arrays to hit a specific wavelength of photoluminescence, which was accomplished, with the three arrays offering a practical red green blue spectrum but also knowledge of the structural nature of homogenous $In_xGa_{1-x}N$.

2.6.4 Chemical Vapor Deposition (CVD)

Centering on the emissions spectrum, researchers focussed on the capability of multi shell nanowires, which had great possibility to offer variation of emissions spectrum without finding out on how to adjust the fluctuating $In_xGa_{1-x}N$ concentration in a single nanowire. To achieve this theory, researcher used a branch of CVD synthesis that is metal organic chemical vapor deposition in order to deposit layers of nanomaterial thin film to acquire a tremendous variation in emission spectra, with diversity in In concentrations $In_xGa_{1-x}N$ of roughly ~1 to 35%. However, their multi shell nature restricted the nanowires composition and causing the formed nanowires to not be pure $In_xGa_{1-x}N$.

Figure 2.6 shows the apparatus set-up for metal organic chemical vapor deposition as reported by Wan *et al*. (2010) in order to synthesize nanowires with variation In composition in the formed nanowires that give the promise of variation of emissions spectrum.

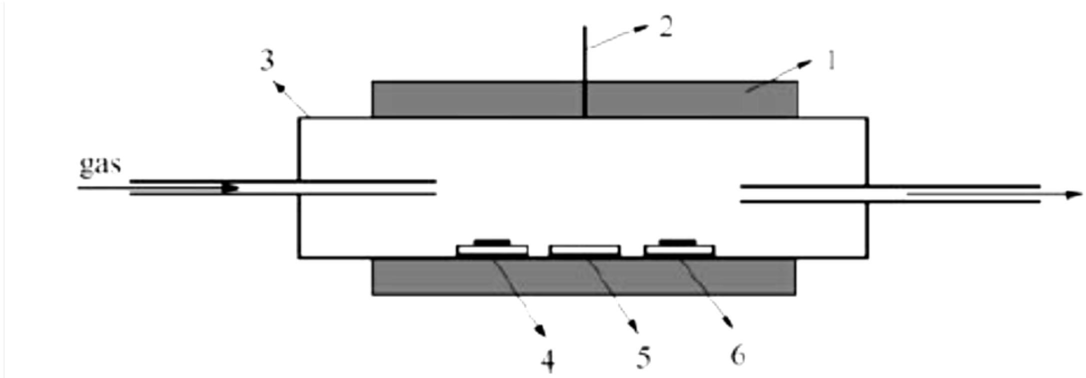

Figure 2.6: Scheme of the experimental system; (1) furnace; (2) thermocouple; (3) quart tube; (4) upstream holder; (5) source boat and (6) downstream holder (Wan et al., 2010).

To successfully execute pure InGaN nanowires synthesis with a higher concentration of InN, Cai *et al.* (2009) used of chemical vapor deposition method, which bypass the problems arise when synthesize using HVPE method. Rather than depend on a halide intermediate to deposit metal source on the substrate surface, the CVD method as reported by Cai *et al.* (2009), positioned both of the metal sources in a quartz tube with silicon substrate, coated with gold as a catalyst. Under low pressure and high temperature, NH_3 and Ar gases were pumped into the tube, during which synthesis of InGaN nanowires took place.

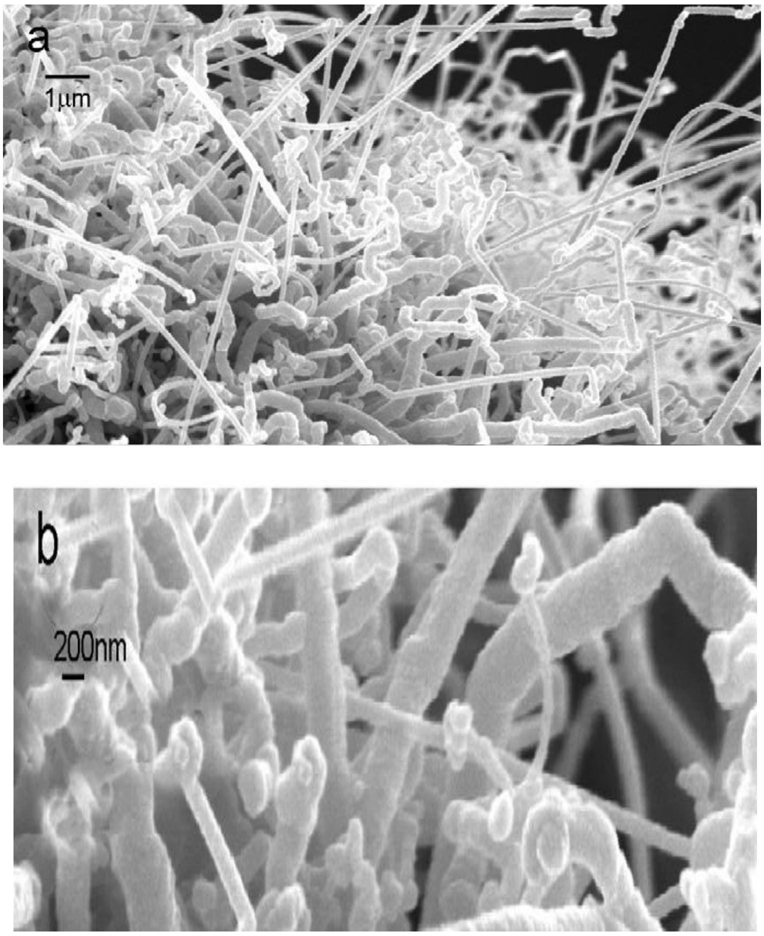

Figure 2.7: Typical low-resolution (a) and high-resolution (b) SEM image of the InGaN nanowires. (Cai *et al.*, 2009)

Cai *et al.* (2009) reported on the successful synthesis of nanowires with relative $In_xGa_{1-x}N$ composition they tried to achieve, however, precise control over the ratios were not very successful. With ratios of nanowires composition stoichiometry increased, Cai *et al.* indicate that no method results on similar to that reported when using HVPE. Hence, while Cai *et al.* (2009) reported that InN fractions in synthesize nanowires are up to 60%, they were actually mixed in with other concentrations available from the composition of formed nanowires.

Figure 2.8 shows the XRD pattern of the InGaN nanowires. With JCPDS 88-2365, 80-0011, 79-2498, 79-2499, both cubic and hexagonal peaks presents with different In compositions can be identified. It it also found that the formed InGaN nanowires are a mixture of hexagonal and cubic phase with different In compositions. These results are further confirmed with the TEM results.

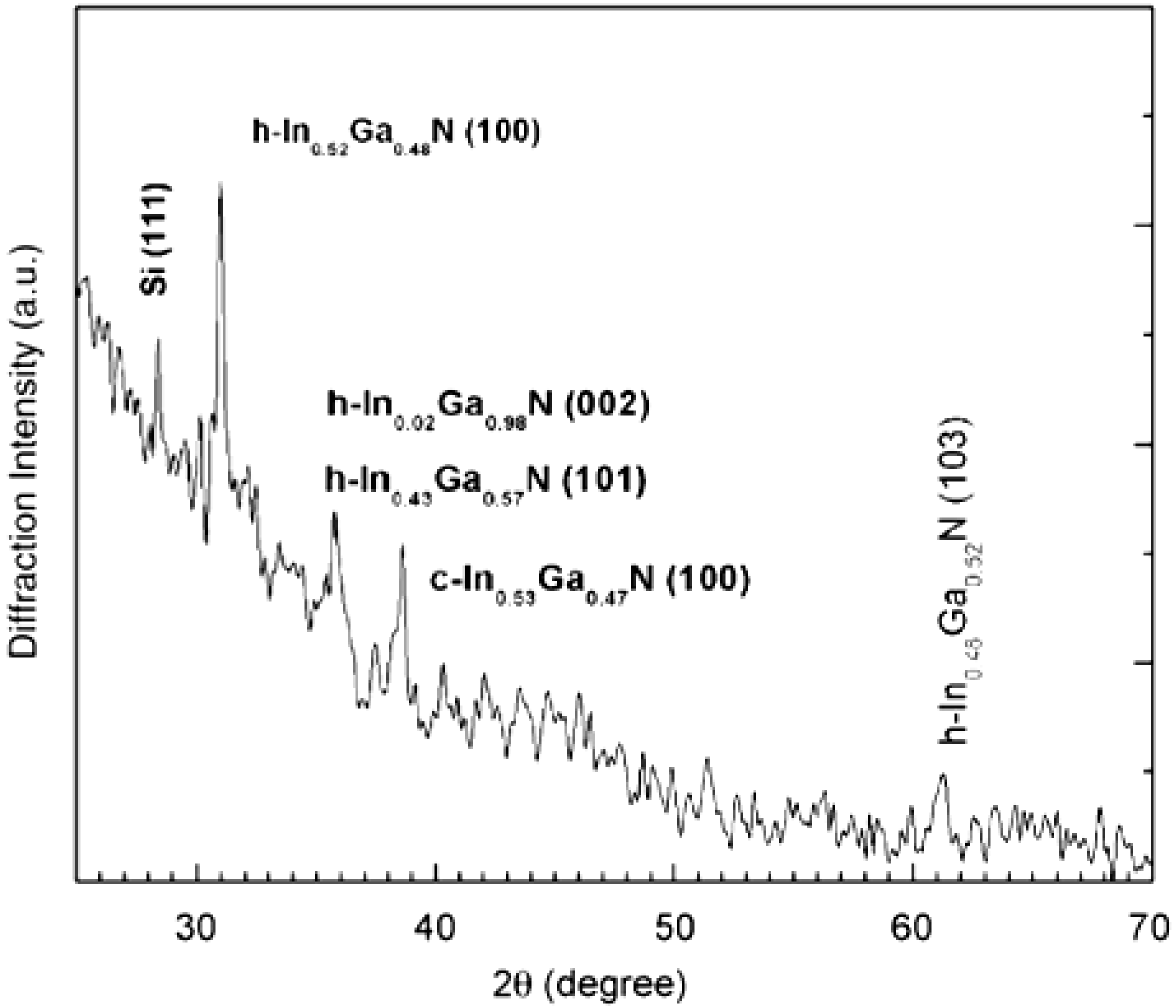

Figure 2.8: XRD pattern of the InGaN nanowires (Cai et al., 2009).