SYNTHESIS OF InN, GaN AND InGaN NANOPARTICLES BY A CHEMICAL METHOD AT LOW TEMPERATURE FOR SOLAR CELL APPLICATIONS

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by

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DEDICATION

I would like to dedicate this work to the soul of my father who passed away while I was doing my research. I also dedicate this work to my mother whose prayers have given me the strengths to complete this work.

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LIST OF ABBREVIATIONS

1-D	One-dimensional
3-D	Three-dimensional
AlN	Aluminum nitride
CVD	Chemical vapor deposition
DAAD	Dielectrophorsis assisted assembly deposition
FESEM	Field emission scanning electron microscopy
RF	Radio frequency
GaN	Gallium nitride
HCP	Hexagonal closed packed
HCVD	Halide Chemical vapor deposition
HEMT	High electron mobility transistor
HNO_3	Nitric acid
HR-XRD	High resolution X-ray diffraction
HT	High temperature
HVPE	Halide vapor phase epitaxy
InGaN	Indium gallium nitride
InI_3	Indium Triiodide
InN	Indium nitride
JCPDS	Joint committee on powder diffraction
LDs	Laser diode
LEDs	Light emitting diodes
Li_3N	Lithium nitride
LT	Low temperature

MBE	Molecular beam epitaxy
MCVD	Metal chemical vapor deposition
MIS	Metal insulator semiconductor
MOCVD	Metal organic chemical vapor deposition
MOCVD	Metal organic chemical vapor deposition
MOS	Metal oxide semiconductor
MQW	Multiquantum-well
MSM	Metal Semiconductor Metal
MVPE	Metal vapor phase epitaxy
NBE	Near band edge emission
NBs	Nanobelts
NCs	Nano cubes
NH4OH	Ammonium hydroxide
nm	Nanometer
NNs	Nano-needles
NPs	Nanoparticles
NRs	Nanorods
NSs	Nanosheets
NTs	Nanotubes
NWs	Nanowires
OAc	Oleic acid
OAm	Oleylamine
OLEDs	Organic light emitting diodes
PAMBE	Plasma assisted molecular beam epitaxy
PA-MOMBE	Plasma assisted metal organic molecular beam epitaxy

PET	Polyethylene terephthalate
PL	Photoluminescence
PPM	Standards part per million
PV	Photo voltaic
PVD	Physical vapor deposition
RE	Red emission
sccm	Standard cubic centimeters per minute
SE	Secondary electrons
TEM	Transmission electron microscopy
TPP	Tri-PhenylPhosphine
UV	Ultraviolet
VLS	Vapor liquid solid

LIST OF SYMBOLS

a,b,c	Lattice constant
Au	Gold
χ	Electron affinity
D	Diffusion coefficient
d	Inter planar spacing
D	Mean crystal size
e	Charge of electron
E_d	Activation energy
E_g	Energy gap
eV	Electron volt
ϕ_B	Schottky barrier height
ϕ_M	Metal work function
ϕ_σ	Semiconductor work function
h	Blank constant
hkl	Miller indices
I_m	Maximum current
I_{sc}	Short circuit current
K	Boltzmann's constant
Mg	Magnesium
Ni	Nickel
^oC	Celsius temperature
P_m	Maximum power

R	Resistance
Si	Silicon
T	Absolute temperature
V_m	Maximum voltage
V_{oc}	Open circuit voltage
Ω	Ohm
x	Indium mole fraction
θ	Diffraction angle
λ	Wavelength

SINTESIS PARTIKEL NANO InN, GaN dan InGaN MELALUI KAEDAH KIMIA PADA SUHU RENDAH UNTUK APLIKASI DALAM SEL SOLAR

ABSTRAK

Kajian ini mengkaji sintesis partikel nano InN, GaN, dan InGaN (NPs) dengan kaedah kimia pada suhu rendah bagi diaplikasikan dalam sel solar. Bagi menjalankan kajian ini, para pengkaji telah menggunakan beberapa konsep teori dan persamaan yang relevan. Proses yang dilaksanakan, termasuklah tindak balas bahan dalam penyejat berputar, pengacau bermagnet, pengemparan, dan proses salutan berputar untuk mendepositkan partikel nano bagi fabrikasi sel solar. Larutan Oleyamine (OAm) digunakan semasa tindakbalas sebagai bahan pelarut. HNO_3 dan NH_4OH digunakan sebagai sumber Nitrogen untuk mensintesis InN, GaN, dan InGaN (NPs). Dua jenis sel solar yang difabrikasi, iaitu: pertama, sel solar heterosimpang (n-InN/P-Si) dan (n-GaN/P-Si), yang menggunakan Si p (111) sebagai substrat, kedua, sel solar homosimpang (n-InGaN/p-InGaN) yang menggunakan Polyethylene terephthalate PET sebagai substrat. Sintesis InN/GaN/InGaN (NPs) dicirikan oleh Field Emission Scanning Electron Microscopy FESEM, Energy Dispersive X-ray Spectroscopy EDX, Transmission Electron Microscopy TEM, X-ray Diffraction XRD, Photo-Luminescence PL, Raman Spectroscopy, dan UV Spectroscopy, di mana sel solar yang difabrikasi dicirikan dengan menggunakan Keithely 2400 electrometer di bawah simulasi cahaya matahari pada 30 mW/cm^2. Partikel nano InN, GaN, dan InGaN disintesis pada masa dan suhu yang berbeza, dan keputusan terbaik diperoleh pada (12jam) di mana suhu 90°C merupakan faktor utama dalam sintesis ini. Teknik salutan berputar mendepositkan

diameter purata saiz fasa partikel nano bagi InN ialah 45nm, GaN 51nm, dan InGaN 19.25nm. Jurang tenaga partikel nano InN yang disintesis adalah 0.97 eV. Di bawah pencahayaan (30 mW/cm$^{2)}$, sel solar heterosimpang n-nN/p-Si (111) memaparkan arus litar pintas 1.2 mA dan kecekapan penukaran sebanyak 1.09 %. Manakala, n-GaN NPs/Si (111) menghasilkan sel solar heterosimpang dengan faktor isi 0.56 dan kecekapan penukaran sebanyak 2.06%. Dalam kajian ini, InGaN didopkan dengan Magnesium (Mg), di mana kepekatan lubang, kerintangan , dan mobiliti telah dikaji. Pengukuran kesan Hall menunjukkan bahawa kepekatan lubang InGaN NCs didopkan dengan Mg meningkat daripada 6.2 × 10^{16} kepada 2.3 × 10^{18} cm^{-3}, manakala mobiliti lubang berkurangan daripada 0.92 kepada 0.1 cm^2/(V.s) apabila nisbah pendopan Mg meningkat daripada 0.005 kepada 0.025 cm^{-3}. Sel solar homosimpang InGaN terbaik yang difabrikasi daripada InGaN nano kiub mengandungi 0.4 Indium pada substrat fleksibel menunjukkan ketumpatan arus litar pintas 12.47 mA/cm^2, voltan litar terbuka (V_{oc}) 0.48 V dengan 54% faktor isi dan 1.19% kecekapan penukaran (η). Kajian ini menunjukkan suatu cara yang jelas untuk mensintesis InN, GaN, InGaN (NPs), dan kemampuannya yang boleh diaplikasi pada sel solar.

SYNTHESIS OF InN, GaN and InGaN NANOPARTICLES BY A CHEMICAL METHOD AT LOW TEMPERATURE FOR SOLAR CELL APPLICATIONS

ABSTRACT

This study examined the synthesis of InN, GaN, InGaN nanoparticles (NPs) by a chemical method at low temperature in order to use in solar cell applications. To carry out this, the researcher has employed a number of relevant theoretical concepts and equations. The processes, which were performed, included the materials reaction in the rotary evaporator, stirrer magnetism, centrifugation, and spin coating process to deposit the nanoparticles for fabricating solar cells. Oleylamine (OAm) solution was used during the reaction and it played the role as a solvent. HNO_3 and NH_4OH were used as a Nitrogen source to synthesize InN, GaN, InGaN (NPs).The fabricated solar cell including two types of solar cells: the first type is hetero-junction solar cell (n-InN/P-Si) and (n-GaN/P-Si) which use Si p-(111) as a substrate, the second type is homo-junction solar cells (n-InGaN/p-InGaN) where Polyethylene terephthalate PET used as substrate. The synthesis of InN/GaN/InGaN (NPs) materials was measured and characterized by Field Emission Scanning Electron Microscopy FESEM, Energy Dispersive X-ray Spectroscopy EDX, Transmission Electron Microscopy TEM, X-ray Diffraction XRD, Photo-Luminescence PL, Raman Spectroscopy, UV-spectroscopy, where the fabricated solar cell characterized by using Keithely 2400 electrometer under simulated sun light at 30 $mW/cm^{2.}$.InN, GaN, and InGaN NPs were synthesized under different times and temperatures, and the best results were found at (12h) where the 90°C was the important key factor in this synthesis. The spin coating technique deposited the nanoparticles with average diameter of the

nanoparticle size phases are 45, 51 and 19.25 nm of InN, GaN and InGaN respectively. The energy gap of the synthesized InN nanoparticle is approximately 0.97 eV. Under illumination (30 mW/cm^2) the n- nN/p-Si (111) hetro-junction solar cells displayed a short circuit current of 1.2 mA and power-conversion efficiency of 1.09%. While, the n-GaN NPs/Si(111) produced a heterojunction solar cell with fill factor of 0.56 and conversion efficiency of 2.06%. In this work, InGaN was doped with Magnesium (Mg) where the hole concentration, resistivity and mobility are studied. The Hall effect measurements showed that the hole concentration of InGaN NCs doped with Mg increase from 6.2 × 10^{16} to 2.3 × 10^{18} cm^{-3}, while the hole mobility to decrease from 0.92 to 0.1 cm^2 /(V.s) as the Mg doping ratio increases from 0.005 to 0.025 cm^{-3}. The best InGaN homo junction solar cell made of nano-cubes film containing 0.4 Indium on flexible substrates showed a short-circuit current density of 1.247 mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.48 V with 54% fill factor and 1.19 of converted efficiency(η). This work resulted in drawing a clear picture of the synthesis of InN, GaN, InGaN (NPs) characteristics and its ability to contribute in solar cell application.

CHAPTER 1: INTRODUCTION

1.1 Overview of the study

Indium gallium nitride (InGaN) is a semiconductor material that contains indium and gallium elements from the third group in the periodic table, which are combined with nitrogen. InGaN is very promising material because its band gap can be shifted by varying its composition [1]. The ternary nitride composition is usually written as $In_xGa_{1-x}N$, with *x* indicating the mole fraction of Indium in the alloy. Over the years, III-nitrides have developed to be new promising materials for optoelectronic and electronic applications [2]. The component of III-nitride, i.e. GaN and its alloys, can be used as the active region of the visible light emitting diode and laser diode because the emission wavelength of InGaN alloy covers the whole visible light range from ultraviolet to infrared. And hence, InGaN alloy has extensive commercial applications such as reading, writing on high volume digital versatile disk (DVD), full-color screen, optical communication [3].

There are various features of GaN and its alloys which include high electron mobility, elevated thermal conductivity, broad and direct band gap (3.4eV). Other features are better chemical stability and high breakdown field, due to relatively stable physical properties. These properties make it suitable for several optoelectronic applications such as short-wavelength optical devices [4], sensing [5], field-emission [6], light-emitting diodes , thermo-electrics [7], and energy conversion photovoltaic solar cell [8, 9]. GaN and its alloys are also suitable materials for fabricating photo-detectors which tend to work in the ultraviolet and visible parts of the solar spectrum [10]. GaN is particularly important as source material for the manufacture of blue and UV light emitters in optoelectronics [11].

In previous research, a plethora of growth methods have been developed to synthesize III-nitrides. The most common methods are molecular beam epitaxy (MBE) [12], thermal ammunition [13], sol–gel chemistry [14], combustion method [15, 16], and metal organic chemical vapor deposition (MOCVD) [17]. Despite the fact that these methods are used for synthesizing III-nitrides, the synthesis of high quality InGaN remains a difficult process, largely as a result of the huge disparities in the lattice constants and variations in the binding energies of GaN and InN. To deal with these limitations, nanostructured InN and GaN have been synthesized from their individual oxides [18], halides [19] or pure metals [19, 20] via different approaches that include ammonolysis [21], laser ablation [22], and several other unconventional methods [23]. In contrast, several researchers in recent years [24-30] have tended to use chemical methods in synthesising nano-particles of different materials such as silver and gold. Interestingly, they claimed that Oleylamine (OAm) is the key factor for synthesizing nanoparticles. The researchers achieved a great success in synthesis of the Magnetic Iron Oxide and FePt Nanoparticles by using OAm, which were applied in many applications [31, 32].

1.2 Motivations for doing the study

The solar cells manufactured nowadays are basically not effective enough to compete with fossil fuels. Furthermore, it has been noticed that the fabrication of solar cells is presently too expensive to generate electricity on a large scale. Nonetheless, the advances of nanotechnology in the manufacture of solar cells have provided access to the production of solar cells a relatively cheaper and more efficient rate. This is deemed to be successful based on the facts given in the following paragraphs.

Solar cells which consist of semiconductor materials, usually silicon electric field, can be launched as a diode, which simply permits the flow of electrons in a solitary direction. The incidence of light on the cells is followed by their absorption of photon energy. The absorbed energy agitates electrons present in the silicon due to the dopant added to the silicon like phosphorus or boron. Due to the intrinsic inefficiency of conventional silicon solar cells (approximately 10%), which is a major drawback, the cost of manufacturing silicon solar cells increases. This is because the incident photons, or light, are required to contain energy higher than that of the band gap, in order to displace an electron. The residual energy is dissipated as heat. In contrast, relatively lower energy of the photon compared to the band gap energy causes the incident photons to pass through the silicon but does not displace an electron. This phenomenon explains the cause of approximately 70% loss in the radiation energy incident on the cell.

Nanotechnology has been put forward as a viable alternative to the conventional techniques of manufacturing solar cells, due to its potential ability to enhance the efficiency of solar cells as well as lower the manufacture expenses. The nanostructure of generating electrons via the absorption of light of a specified wavelength. Electron flow through the nanostructure is maintained until they arrive at the aluminum contact where they are merged to generate current in the external circuits. This nanostructure of cell is relatively less expensive to manufacture than conventional silicon solar cells. Their manufacture process also does not demand the use of costly equipment such as clean rooms or vacuum chambers.

In view of the fact that the manufacturing expense of conventional solar cells is one of the main disadvantage, this novel of nanotechnology is capable of

manufacturing low power devices with adequate energy. It would help to preserve the environment and supply power to country sides or third world countries. The novel nanotechnology has also an extensive range of industrial applications. In addition, inexpensive solar energy can be ideally used to generate light, manufacture devices used in the health sector, heat up water, and cooking. Finally, inexpensive solar cells could also revolutionize the electronics industry. The positive impact of nanotechnology in the society is enormous.

1.3 Statement of the problem

With reference to previous studies, the most common methods used to synthesize III-nitride nanoparticles or thin films are molecular beam epitaxy (MBE) [12], thermal ammunition [13], combustion method [15, 16], and metal organic chemical vapor deposition (MOCVD) [17]. However, several researchers in recent years [24-30] have shown interest in using chemical methods in synthesizing nanoparticles of different materials such as silver and gold. Interestingly, these recent researchers have claimed that OAm is the key factor for synthesizing nanoparticles elements because OAm plays the roles of both stabilizing agents and reduction. Also, the OAm optimizes the reaction conditions more significantly compared to more complex multicomponent systems [33]. By using OAm, researchers have synthesized Magnetic Iron Oxide and FePt Nanoparticles which were applied in many applications [31, 32].

Compared to the previous techniques used to synthesize InN, GaN, and InGaN or thin films, the contemporary techniques did not use OAm. The big challenge here is very much related to the use of OAm in the synthesis of InN, GaN, and InGaN, taking into account the role of OAm in nanoparticle synthesis. Therefore,

there is a need to use an easy way to synthesize InN, GaN and InGaN by lowering the synthesis temperature using OAm a surfactant. In this study, the InN, GaN and InGaN NPs are obtained when HNO_3 and NH_4OH are added to the solution at 90˚C. The experiments use OAm as the main factor in the provision of an intense reducing environment for the thermal disintegration of $In(AcAc)_3$ and $Ga(AcAc)_3$. Furthermore, OAm is applied as a surfactant to generate nanoparticles of large aggregates distribution. Nanoparticles are achieved by the decomposition of $In(AcAc)_3$ and $Ga(AcAc)_3$ in OAm.

This study is a bridge between the famous techniques (i.e., MBE, MOCVD,…) used to synthesize InN, GaN and InGaN NPs and the recent chemical methods used to synthesize nanoparticle elements such as silver or gold nanoparticles. This research was devoted to produce InN, GaN, and InGaN for the first time using an effective solvent OAm to reduce $In(AcAc)_3$ and $Ga(AcAc)_3$. This work uses the OAm as a main factor in the provision of an intense reducing environment for the thermal disintegration of In $(AcAc)_3$ and $Ga(AcAc)_3$. Furthermore, OAm is applied as a surfactant to generate nanoparticles of large aggregates with a narrow size distribution.

For the solar cell device, many researchers have started to produce flexible solar cells [34-37] that can be installed on un-flat walls because they are light and flexible. Ouyang and Yang in 2006 used D-sorbitol to make a good adhesion between the LED device layers, where the D-sorbitol achieved a conducting transparent and electric glue [38]. In this research the InGaN nanoparticles will be deposited on PET substrate. D-sorbitol will be used to make adhesion of NPs with the PET substrate for the first time in the fabrication of the homojunction flexible

solar cells. Thus, this study introduces a simple and easy method for the synthesis of InN, GaN and InGaN NPs. This method is considered a novel contribution because it does not require high temperature condition or/and vacuum/gas environment. The chemicals used in this method are relatively cheaper than those currently used in the industries to synthesize InN, GaN and InGaN NPs. In addition to these features, this chemical method can effectively facilitate the synthesis of nitride compositions.

The materials used to synthesize InN, GaN and InGaN nanoparticles comprise Oleylamine (OAm) (as a solvent), acetylacitonate materials like Indium acetylacetonate and Gallium acetylacetonate will be used. HNO_3 and NH_4OH are used as the nitrogen sources.

1.4 Scope of the study

In this study, InN NPs and GaN NPs were synthesized under different temperatures and time conditions so as to choose the best parameters' values. These best values were used in fabricating n-InN/p-Si and n-GaN/p-Si hetero junction solar cells. The p-type Si was used as the absorber layer.

The best parameters values of time and temperature were used to synthesize InGaN NPs/ NCs. In InGaN NCs, the effect of the layer thickness, the electrical characteristics of p-type InGaN NCs doped by Mg were studied. Indium ratio of InGaN NCs was also studied to be used in n-InGaN/p-InGaN homo junction solar cells fabrication.

1.5 Research objectives

In order to synthesize InN, GaN and InGaN NPs using OAm as a surfactant for the first time, a chemical method was established under normal conditions and

without the need to vacuum. This resulted in the achievement of effective low cost fabrication of solar cell. The following specific objectives have been formulated to guide the present study:

1. To synthesize and characterize InN, GaN, and InGaN nanoparticles (NPs) produced by a chemical method at low temperature using Oleylamine (OAm) as a surfactant.
2. To fabricate and study the parameters of heterojunction solar cells n-InN/p-Si and n-GaN/p-Si, and homojunction solar cells n-InGaN/P-InGaN on flexible PET substrate.
3. To investigate the effectiveness of D-sorbitol on adhesion between the nanoparticles NPs layer and PET.

1.6 Originality of the study

The originality of this study is using OAm for the first time to synthesize InN, GaN and InGaN in order to reduce the high temperature required in other techniques. This work includes three key points. Firstly, the synthesis of InN by chemical method technique under different times has been done, then the best time result used in solar cell fabrication. Secondly, the synthesis of GaN by using a chemical method technique under different parameters such as time, temperatures and doubling the nitrogen gas source. The best parameters result has been used in solar cell fabrication. Finally, the best time and temperature values of InN and GaN synthesis were applied to synthesize InGaN by the same technique. In this key point the indium mole fraction of InGaN has been studied and applied in solar cell fabrication.

1.7 Thesis outline

This thesis is structured into eight chapters. The first chapter introduces the topic of the study. In addition to this, InN, GaN, InGaN significance, the justification of the study, a new InN, GaN, InGaN synthesis method, and the objectives of this study are discussed in the first chapter. The second chapter presents a comprehensive review of related literature on the growth and synthesis of InN, GaN, and InGaN. It also provides an overview of InN, GaN, InGaN and its application in solar cells as well as a brief synopsis of OAm and acetylacetonate $(AcAc)_3$ groups used in the synthesis of nanoparticles. The third chapter presents some theoretical equations to describe the mechanism of chemical reactions. P-n junction fundamentals are also discussed in this chapter. The fourth chapter gives a detailed explanation of the method used to synthesize InN, GaN, InGaN nanoparticles and solar cell fabrication. The characterization techniques were also dealt with in this chapter. The fifth chapter focuses on various experiments that were carried out to characterize the InN NPs and its applications in the fabricated solar cells which were measured through the solar cell parameters. The sixth chapter describes all experiments used to characterize the GaN NPs and its application in the fabricated solar cells which were measured through the solar cell parameters. The seventh chapter provides a detailed characterization and analysis of the InGaN NCs and its application in solar cells. All the solar cells parameters were measured in the NOR laboratory in the School of Physics. The eighth chapter presents the conclusions of this study. Some recommendations and suggestions for future research are also dealt with in this chapter.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

This chapter reviews previous studies with a focus on the methods used to prepare InN, GaN and InGaN. These methods include: MBE, MOCVD, RF Sputtering, HVPE, PAMBE, HCDV, and MCVD. This is followed by description of several applications of InN, GaN and InGaN such as solar cell and LED. This chapter also describes some studies related to the use of simple chemical methods for the preparation of nanoparticles. Generally, this chapter bridges the gap between the techniques (such as MBE, MOCVD…) and chemical methods used in the preparation of compound materials.

2.2 Background of InN, GaN, InGaN nano structure growth technique

2.2.1 InN and GaN nano structure growth technique

In early years of the 19^{th} century, GaN was effectively synthesized as a semiconductor material via the transmission of NH_3 gas over molten metallic Ga at temperatures exceeding 700°C by Johnson et al. (1932)[39]. Pankove et al. (1971) [40] were the first to devise an LED with insulating to n-type structure using GaN; however the material was of quite low quality and hindered by large enclosing background electron concentration derived from native defects generally believed to be nitrogen vacancies. However, Pankove studies ran into considerable drawbacks in obtaining high-quality material. GaN quality was drastically improved by Yoshida et al. (1983) with the introduction of an AlN buffer layer that aided the nucleation and smoothening on GaN films [41]. Subsequent studies carried out in the 1983s-1995s placed emphasis on the synthesis of p-type GaN under variable experimental conditions [42, 43].

For instance, Matsuoka et al. (2002) synthesized wurtzite InN films on GaN layer using metalorganic vapor phase epitaxy (MVPE) [44]. The strong photoluminescence (PL) energy band gap (0.76eV) observed at room temperature with high power excitation at ≈1.9eV was reported as the band gap of the polycrystalline films. Thus, Matsuoka and his co-workers suggested that a wurtzite InN single crystal exhibit a factual band gap of 0.7–1.0eV, with a difference that could be attributable to the variation in crystallinity [45]. Furthermore, Xiao et al. (2005) synthesized InN films of high quality crystallinity on sapphire substrates via radio-frequency plasma-excited molecular beam epitaxy (RF-MBE) [44]. Xiao and his workers reported that the InN films (InN buffer layer) synthesized with high temperature (HT) exhibited lower quality than those with low temperature InN buffer layer [44]. In another study, Chen et al. (2006) synthesized InN nanorods on Si(111) substrates by means of plasma-assisted molecular-beam epitaxy (PAMBE) at variable temperature conditions (LT- and HT-InN nanorods). The nanorods were found to be hexagonally shaped, distinct and compactly distributed on the substrate [46].

Further advances in the application of GaN in the past two decades were developed from the steady innovations in the fabrication and characterization of progressively smaller structures. These advances in material processes and in the theoretical investigation of nanoscales phenomenon include several experimental techniques which offer enormous opportunities for the growth of distinctive nanostructured materials. The fabrication of low dimensional structure certainly provided a number of diverse physical properties that include electronic structure, morphology, quantum tunneling, surface effect, quantum phase transition, quantum size-effect confinement, and nonlinear susceptibility enhancements [47, 48].

In relation to the available diverse nanostructures such as nanowires (NWs) have garnered the most interest for future nanotechnology applications in the field of electronic and optoelectronic devices. GaN is of particular significance because it has been shown to be a source material for high-quality NWs [49] and can be either grown intrinsically n-type or doped p-type via magnesium inclusion during growth [50]. In addition, one dimensional (1D) nanostructures manufactured with GaN such as nanowires (NWs), nanorods (NRs), nanotubes (NTs) and nanobelts (NBs), within the scale of small diameters are characterized by considerably different optical, electrical and magnetic properties compared to their bulk three-dimensional (3D) crystalline structure [51].

In the last 10 years, enormous amount of research has been devoted to the epitaxial growth of GaN nanostructures with different shapes using a range of growth techniques [8, 52, 53]. The foremost successful fabrication of GaN NWs was carried out by Han et al. (2004) [54].

Furthermore, Ke et al. (2010) synthesized high density InN/GaN nano-dots by means of pulsed mode (PM) metal–organic chemical vapour deposition (MOCVD) at 550°C growth temperature, which was achieved due to the high NH_3 flow rate generated at the growth surface. In addition, the high carrier concentration thermally agitated to the conduction band, due to high In vacancy (V_{In}) in the InN nano-dots [55]. The GaN layer (2.5 μm thick) was grown at 1000°C on Low temperature (LT) GaN/InN/sapphire template, where GaN layer (LT) protects the InN layer from direct exposure to hydrogen flow during high temperature (HT) GaN growth. The underneath InN layer of approximately 100 nm was grown on sapphire c-plane using

a metal-organic chemical vapor deposition (MOCVD) system. The synthesized columnar structured LT GaN and HT GaN exhibited good crystallinity [56].

Similarly, Singh et al. (2013) developed a simple method for controlling crystalline quality and morphology of InN, which involved the in-situ deposition of a buffer layer of indium oxide on Si substrate using atmospheric pressure-halide vapour phase epitaxy before growing InN. The results of the synthesis have shown that the buffer layer of indium oxide helps in the growth of indium nitride nano-petals [57].

Kuo et al. (2011) synthesized nanostructured indium nitride (InN) films on the c-plane sapphire substrate using the Plasma Assisted Metal Organic Molecular Beam Epitaxy (PA-MOMBE) system[58]. Kuo et al. confirmed the possibility of synthesizing InN film with two dimensional growth mode at 500°C. The films exhibited high orientation along the c-plane. As the growth temperature of 700°C is attained, the films exhibited randomly oriented crystalline nature of (InN) 1D nanostructures. Furthermore, the enhancement of the indium atoms' surface mobility at high growth temperature was found to be crucial to the formation of InN nanonails and nanorods [59].

Several research groups have synthesized nano-InN using various methods, such as ammonolysis, solid-state metathesis reactions [60-62], and solvo-thermal autoclave methods [63]. For instance, Cumberland et al. (2001) used InI_3 and Li_3N as starting materials and mediated the speed of the reaction by adding different proportions of $LiNH_2$ and NH_4Cl to the reaction. The exchange in reactions between gallium triiodide (GaI_3) and lithium nitride (Li_3N) produces crystalline gallium nitride (GaN) in seconds at ambient pressure by the addition of lithium amide

($LiNH_2$) and ammonium chloride (NH_4Cl) to metathesis. In this reaction enables both the reaction velocity and temperatures to be measured as the additives, the GaI_3/Li_3N reaction propagates at >100 cm/s with a reaction temperature above 1000°C, which exceeds the 850°C decomposition temperature of GaN. Applying the concepts developed in the synthesis of GaN, crystalline InN has been synthesized for the first time using solid-state metathesis reactions. By using a specially designed thermal dissipation cell, the yield of GaN can be increased up to 78.8%. [60].

Ammonolysis reactions are carried out in a tube furnace where the indium source is held in a ceramic boat, and ammonia gas is passed over it at high temperature. At temperatures above 1000° C, ammonia cracks into a highly reactive nitrogen spaces. This method converts oxides to nitrides so indium oxide nanopowders are typically used as a starting material [64]. Ammonolysis has also been tried on ammonium fluoride-based precursors, with the primary objective of synthesizing InGaN [61]. Although this technique is analogous to the above mentioned one, it reported only the formation of wurtzite InN at temperatures more than 550°C despite the presence of Ga in the original precursor. It was also noted that the hexagonal InN displayed no visible luminescence.

For solar cells applications, it is imperative to employ fabrication techniques of III-N semiconductors, such as physical vapour deposition (PVD) via the thermal evaporation of solid materials and thermal CVD using a horizontal tube furnace (HTF). These methods of synthesizing GaN were deemed the least in terms of cost of operations along with simplicity of experimental design [8, 52, 65], because Tang and his team fabricated the heterojunction between n-GaN nanowires (NWs) and p-cuprous oxide (Cu_2O) (111) which was fabricated vertically by thermal evaporation

of GaN conventional powders without using any catalyst or template. To grow GaN NWs flowers directly on catalysis-free Si (111) via thermal evaporation of GaN powder in NH_3 free environments, Saron and Hashim presented a simple and low cost physical vapor deposition (PVD) method. Recently, Ghazali et al. (2014) successfully synthesized Gallium nitride (GaN) nanostructures via the combination of Ga_2O_3, HCl, NH_4OH, and H_2O for 2 h using electrochemical deposition technique. The deposited Ga_2O_3 sample was subsequently ammoniated in a horizontal furnace at different ammoniating durations and temperatures at (850 and 900)°C [66]. All the methods used in previous studies require high temperature, costly instrument, and costly substrate like silicon. Therefore, a low temperature technique for the preparation of GaN nanoparticles is idealy required for a large scale synthesis.

2.2.2 InGaN nano structure growth technique

Several studies have been carried out to resolve the various constraints that limit InGaN growth. For example Brandt et al. (2003) developed a simple approach via plasma-assisted molecular-beam epitaxy (PAMBE) to decrease the impact of surface segregation of In during the growth of (In,Ga)N/GaN multiple quantum wells, which simultaneously causes abrupt interfaces. The approach entails the use of a elevated substrate temperature than normally applied, as well as the inclusion of N-rich compounds in the synthesis route and Ga-stable materials during growth of the barrier [12].

Kuykendall et al in 2007 report for the first time the growth of single-crystalline $In_xGa_{1-x}N$ nanowires across the entire compositional range from x =0 to 1; the nanowires were synthesized by low temperature halide chemical vapour deposition(HCVD) and were shown to have tunable emission from the near-

ultraviolet to the near-infrared region. They propose that the exceptional composition tunability is due to the low process temperature and the ability of the nanowire morphology to accommodate strain-relaxed growth, which suppresses the tendency toward phase separation that plagues the thin film community [67]. Liu et al in 2014 demonstrated the catalytic growth of $In_xGa_{1-x}N$ ($0.10 \leq x \leq 0.17$) nanocolumn arrays with high crystallinity on silicon substrates using metal–organic chemical vapor deposition (MOCVD) with trimethylindium (TMIn), triethylgallium (TEGa), and ammonia as precursors. The high quality of InGaN nanocolumns (NCs) were obtained due to the utilization of TEGa that achieved less carbon impurities and offered more comparable vapor pressure with that of TMIn at low temperature. Furthermore, the bandgap of this InGaN can be modulated from UV to visible region simply by tuning the ratio of the precursor during the fabrication [68]

Hong et al. (2009) used plasma-assisted molecular beam epitaxy (PAMBE) to fabricate InGaN/GaN hetero-structure nano-rods without embedded quantum well QW-active layers. A study of the emission processes showed that vertically-aligned $In_{0.11}Ga_{0.89}N$/GaN-hetero-structure nanorods are capable of emitting roughly one order magnitude more intense of green light compared to $In_{0.13}Ga_{0.87}N$ film [69]. In 2010, Wu used molecular beam epitaxy to grow InGaN nanorod arrays on bare and high-temperature AlN-buffered Si (111) substrates. The good vertically alignment of the InGaN nanorod arrays is attributed to the high-temperature AlN buffer layer. High-resolution transmission electron microscopy identified an amorphous SiNx layer synthesized on the bare Si substrate at the interface. Thus, it was deduced that the thickness and flatness of the SiNx layer may influence the relative alignment of the nanorods with the substrate, and the interface quality and uniformity of the

synthesized InGaN nanorods were enhanced with high-temperature AlN buffer layer [70].

Based on the growth mode of vapor-liquid-solid (VLS), Chang et al. (2002) synthesized InGaN nano-needles (NNs) via the spiral deposition of InGaN with a quasi-periodical arrangement of indium material in the direction of growth. This VLS growth was applied in Metalorganic Chemical Vapor Deposition (MCVD) with Au nanoparticles (NPs) catalyzing the reaction, where the Au NPs were produced on a GaN template by means of the pulsed laser irradiation. The alternating indium content along the growth direction is attributable to the quasi-periodically pulsed actions involved in indium super-saturation in the dissolved Au NP at the peak of InGaN NNs. The growth of a quasi-one-dimensional structure can be activated without difficulty because the spiral deposition of InGaN is associated with the creation of NNs at the site of Au NPs with a screw-type dislocation below the GaN template [71].

Gopalakrishnan in (2012) developed a basic technique for the growth of gallium nitride (GaN) and indium gallium nitride (InGaN) nanoparticles (NPs) using a straightforward chemical co-precipitation method. The mean diameters of the GaN and InGaN NPs were determined at 38 nm and 12 nm, respectively. GaN NPs exhibited a hexagonal structure of high crystalline quality while InGaN NPs were cubic. The synthesis process involved nitridation in a quartz tube reactor under ammonia (NH_3) flow rate of 1000 sccm for 2 h at 950°C [72].

2.3 Overview of InN, GaN, InGaN and its application in solar cell

The synthesis of GaN on Si substrates is characterized by several deep level defects, such as dislocations arising from lattice mismatch, and tensile or compressive strain which may impinge on the effectiveness of GaN-based devices. Thus, a thin layer of crystalline Si_3N_4 or AlN was grown on the substrate via a nitridation to avoid this problem [73, 74]. Recently, Wu et al. (2002) showed the constant variation of energy gap of $In_{1-x}Ga_xN$ alloys from 0.7 to 3.4 eV, based on a full-solar-spectrum material structure for multi-junction solar cells. They also discovered that the optic-electronic properties of these alloys increase their resistance to high-energy (2MeV) proton irradiation compared to the conventional presently utilized photovoltaic materials, for example GaInP and GaAs. Accordingly, Wu et al. (2003) study presented the best possible alternative for radiation-hard high-efficiency solar cells in space applications. The lack of sensitivity exhibited by the semiconductor in reaction to radiation induced defects is due to the location of the band edges in relation to the average dangling bond defect energy defined by the Fermi level stabilization energy in $In_{1-x}Ga_xN$ alloys [75].

Nguyen et al. (2011) studied the synthesis and characteristics of high quality InN nanowires on Si(111) substrates and InN nanowires. By employing an in situ deposited In seeding layer, They have achieved electronically pure, nearly intrinsic InN nanowires directly on Si (111) substrates by molecular beam epitaxy. The growth and characterization of Mg-doped InN nanowires is also investigated, which can display superior structural and optical properties. They have further studied the epitaxial growth, fabrication, and characterization of InN:Si/i-InN and InN:Mg/i-InN/InN:Si axial nanowire structures on p-type and n-type Si(111) substrates, respectively. With the use of a CdS surface passivation, InN:Mg/i-InN/InN:Si

nanowire homojunction solar cells exhibit a promising short-circuit current density of ~14.4 mA/cm2 and power-conversion efficiency of ~0.68% under simulated (AM 1.5G = 100 mW/cm^2) illumination [76].

Reichertz et al. (2009) used MBE to synthesize p- and n-type GaN dual junction solar cell on a standard n-type Si wafer with buffer layer of AlN. They found that Al diffuses into the Si substrate at some point in the synthesis of GaN layers to form silicon solar cell of low series resistance at the GaN/Si hetero-junction [77]. GaN was synthesized on Si, a thin layer of Si_3N_4 is formed by a nitridation of the substrate, which has been shown to be more beneficial for subsequent deposition of GaN than AlN[78]. Lee et al. (2010) reported on the intensity GaN nanowire UV–blue LEDs, manufactured via connecting hetero junctions of n-GaN nanowires and p-GaN substrates by means of random dispersion (RD) and dielectrophoresis assisted assembly deposition (DAAD). These GaN nanowire LEDs are characterized by bright UV–blue emission strong enough to be visibly seen regardless of the quantity of GaN nanowire LED synthesized [79].

The fabrication of III-nitride photovoltaic cell with external quantum efficiency of 63% has been recorded. In_xGa_{1-x} N/GaN p-i-n double hetero-junction solar cells were fabricated on (0001) sapphire substrates with Indium mole fraction of 12% using metal-organic chemical vapor deposition. InGaN was shown to be comprehensibly strained to the GaN buffer layer based on the characteristics of its epitaxial composition. The solar cells parameters include short circuit current density of 4.2 mA/cm^2, fill factor of 75%, and open circuit voltage of 1.81 V under AM_0 illumination. The external quantum efficiency can be enhanced by optimizing the top contact grid [80]. In addition, Tang et al. (2008) similarly synthesized hetero-

junction GaN NRs / n-Si(111) based solar cell diode by CVD with conversion efficiency of 2.73% [8].

In another study, Dahal et al. (2009) have reported characteristics and photovoltaic of InGaN/GaN solar cells which were synthesized using multiple quantum well (MQW). The fabricated solar cells of $In_{0.3}Ga_{0.7}$ N/GaN MQWs showed an open circuit voltage of about 2V, fill factor of approximately 60%, and an external efficiency of 40% and 10% at 420nm and 450nm respectively. Saron et al. (2013) fabricated hetero-junction solar cells of GaN nanostructures on Si substrates by means of thermal chemical vapor deposition (CVD), where the GaN was grown through the direct reaction of Ga vapor and NH_3 solution at 1050°C. The J–V characteristics showed rectifying behavior for the GaN/n-Si junction and Ohmic behavior for the GaN/p-Si junction. Upon illumination (30mW/cm^2), the solar cell devices showed an efficiency of 6.18% [81].

Some other studies have reported the fabrication of solar cell hybrid device n-ZnO/i-InGaN/p-GaN as upturned structures used for hybrid ZnO/nitride solar cells. The p-type GaN was synthesized on a sapphire substrate. Afterwards, i-InGaN and n-ZnO layers were deposited on p-GaN. In addition to reduction in energy conversion efficiency, the development of defects in the p-GaN region during the dry etching process impairs the solar cell device by increasing the series resistance. This problem was resolved by the creation of microrods on the p-GaN, which facilitates the elimination of the weak structure in p-GaN, which in turn drastically decrease the series resistance as well as improve energy conversion efficiency [82]. Young et al. (2014) synthesized InGaN/GaN multiple quantum well solar cells on a bulk (0001) substrate via metalorganic chemical vapour deposition (MOCVD). They improved

the optical coatings in order to augment light absorption in the device using a front-side anti-reflective coating and designing a back-side dichroic mirror to minimize front surface reflections, ensuring the suitability of the cells for multi-junction solar cell. Under AM 1.5 solar application of optical coatings increased conversion efficiency by 37.5% [83].

It can be inferred from the studies reviewed in this section that inexpensive techniques used for the preparation of GaN are still inadequate. This issue demands further investigations to find out other methods which can reduce the cost of synthesizing GaN such as synthesis under atmospheric pressure condition, rather than high temperature condition or vacuum/gas environment, which are more benifit in commercial electronic devices fabrication.

2.4 The chemical synthesizing and fabrication techniques used (Oleylamine, D-sorbitol, and PET)

Most of researchers have recently used OAm to synthesize nano metals because the OAm is an effective solvent in reducing acetylacetonate metals, resulting in further interaction in metal nanoparticles. Thus, OAm is used as a surfactant with indium and gallium acetylacetonate. The required modification involved in this work is to add HNO_3 and NH_4OH to the reaction as a source of nitrogen to synthesize the nitride's compounds nanoparticles. Then, the purification of nanoparticle will be held by using the centrifugation. Yonglan and Luo in 2009 provided details on the synthesis of $CuGaSe_2$ and $CuInSe_2$ as a hexagonal phase in micro-plates by adding copper, indium, and gallium salts and selenium powder as precursors with stoichiometric ratio to the mixture of OAm and oleic acid [84]. Faraj et al. (2011) synthesized layer CIGS by means of two solutions. Firstly, Copper acetylacetonate,

Gallium acetylacetonate, and Indium acetylacetonate were mixed together and dissolved in OAm at room temperature. The second solution was prepared by adding selenium powder to OAm with resulting solution kept at 90°C under vacuum pump for 1 hour; which was subsequently heated to 260°C for 20 minutes and kept at same temperature. 5mL of the first solution was poured into solution 2, and thoroughly mixed under vigorous stirring using a magnetic stirrer. The temperature decreased to 100°C after 30 min. The solution was then re-heated for an hour to attain 260°C. Afterwards, the solution was combined with 5mL of methanol and centrifuged several times at 3300 c/min for 8 min to yield the final product of CIGS nanoparticles ink [85]. Guo et al. (2010) used OAm to creat an appropriate inorganic colloidal nanocrystal ink as a source material for scalable coating in the production of inexpensive solar cells. The study presented a simplistic approach to growth of chalcopyrite ($CuInSe_2$) nanocrystals and confirmed that inks derived from these nanocrystals can be employed to produce simple solar cells of 3.2% efficiency under AM1.5 illumination [86]. In other studies, Ni−OAm complexes were synthesized by Park et al. (2005) via the reaction of $Ni(acac)_2$ with OAm at reasonable temperature (200 and 215)°C, resulting in highly dispersed Ni and NiO nanoparticles. The resultant solution was introduced into TPP (tri-phenylphosphine) under higher heating conditions, which ensures the dispersion of particles in nonpolar solvents such as dichloromethane [25]. A number of researchers have used combined surfactant mixtures (such as OAc, OAm, and hexadecanediol) for NPs synthesis. Their studies revealed that the eventual outline of the particles on the crystal planes is dependent on the binding difference between oleate (salt or ester of oleic acid) and OAm [24]. OAm is also utilized to synthesize Ni-based bimetallic magnetic NPs, such as the asymmetrical NiFe NPs via the decomposition of $Fe(acac)_3$ and

$Ni(acac)_2$. OAm plays the triple roles of solvent, surfactant and reductant. The morphology was enhanced by modulating the introduction of co-surfactants such as dodecanediol [26]. Metin et al. (2011) reported that OAm displays a non-toxic effect on their catalytic activity-dehydrogenation of ammonia−borane [28]. OAm produced isotropic shapes; however it tended to forms highly branched morphologies when mixed with catalyst [27].

Recent carried out studies on simple and large-scale synthesis of silver and gold nano-crystals via reduction of metal precursors in the presence of OAm at high temperature have pointed that this method is independent of time and solvent which consuming the nanoparticle sizes during synthesis steps. Here, OAm plays the roles of both stabilizing agents and reduction. Thus, the OAm optimizes the reaction conditions more significantly compared to more complex multicomponent systems [33]. The very current studies emphasize the flexible function of OAm as a reagent for the synthesis of different nanoparticle systems. OAm also serves as a solvent, surfactant, and reducing agent. In addition, OAm has the specific role either solitarily or jointly with related reactants to synthesise nanostructures using a range of inorganic or organic compounds as preceding reagents. OAm can catalyze the experiment to yield nanoparticles by chelating with the metal ions of the related precursor to form complexes [29].

Ouyang and Yang (2006) fabricated Polymer light-emitting diodes using the lamination process and incorporating the conducting polymer glue (D-sorbitol) as key factor to successfully bring about the adhesion between the LED layers; where they applied a PEDOT:PSS film on a PET/ITO substrate layer 1 (anode in the device) by spin-coating process. Aluminum was deposited on an additional PET

plastic substrate under conditions of high temperature, and a MEH-PPV solution was then spin-coated on this plastic/Al substrate layer 2 (cathode in the device). The cathode and anode were subsequently positioned close to the D-sorbitol layer deposited between the two layers. Pressure was mildly applied on both sides [38].

2.5 Nanoparticles and suface plasmon resonance

Nanoparticle research is currently an area of intense scientific research due to a wide variety of potential applications in biomedical, optical, and electronic fields. Nanoparticles are of great scientific interest as they are a bridge between bulk materials and atomic or molecular structures. Although a bulk material should have constant physical properties regardless of its size, at the nano-scale this is often not the case. Size-dependent properties are observed, such as quantum confinement in semiconductor particles and surface plasmon resonance in some metal particles. The properties of nanoparticles change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant.

The nanoparticles size (nanometer) refers to one billionth order which is a prefix denoting 10^{-9}. The different definitions of nanoparticles vary with the fields, materials, and applications concerned. The particles ranging from 1–100 nm in size could be described as nanoparticles, although their physical properties can differ. The particles within this size range are usually referred to as nanoparticles, and are considered smaller than sub-micron particles, which are less than the visible light wavelength, hence must be analyzed in a different way. As the size of solid particles reduces (micronized), they are more subjective to the behavior of atoms or the molecules and they tend to display properties different compared to those of the bulk solid of the similar material. This is because of changes in bonding state of atoms or

molecules that make up the particles. For instance, a cube consisting of 1 cm in side length is split into a cube of 1μm, the particle number rises to 10^{12} and is divided to the one of 10 nm, then it adds up to 10^{18}, where a fraction of atoms or molecules positioned at the surface of the particles become further active compared to those within the solid particles. This signifies simple bonding with the contacting materials and brings about different changes in particle properties [87].

The idea of surface plasmon enhanced visible light emission. Moreover, the enhancement of an emission rate is also very important for the development of communication technology and optical computing. However, spontaneous emission rates of InGaN-GaN QWs are usually reduced by the quantum confinement. There are only a few reports on the enhancement of the emission rates by reducing the piezo-electric field and making photonic crystal structure [88]. The enhancement in the absorption within the semiconductor results in increased photocurrent response in Si p-n junction diodes over wavelength ranges that correspond closely to the nanoparticle plasmon resonance wavelengths as determined by measuring the extinction spectra. These observations suggest a variety of approaches for improving the performance of p-n junction devices such as photodetectors, imaging arrays, and photovoltaics [89].

In a purely semiconductor-based device structure, electromagnetic radiation incident on the semiconductor gives rise to an optical transition rate that is proportional to the square of the electric field amplitude E_o. Furthermore, the photon traversing a semiconductor is absorbed, resulting in the creation of an electron–hole pair, which is proportional to n/c (where n is the index of refraction of the semiconductor and c is the speed of light in vacuum). This represents the duration of