GROWTH OF GALLIUM NITRIDE NANOMATERIALS BY SOL-GEL DIP COATING METHOD

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2024

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

October 2024

ACKNOWLEDGEMENT

Foremost, I am grateful to Allah SWT our Lord and Cherisher on whom ultimately, we depend for sustenance and guidance. Indeed, without His help and will, nothing is accomplished. First, I want to sincerely thank my supervisor, Assoc. Prof. Dr. Ng Sha Shiong for his unwavering support on my research works. His insightful criticism, tolerance and profound experience have been great value for me throughout this journey of experimental works and writing this thesis. The generous support from the Institute of Nano-Optoelectronics and Research (INOR) laboratory assistants is much welcome. They have given me untiring help during my difficult times in handling laboratory works. With not their assistance, this work would not have come to an end. In addition, I appreciate the help I received from the Ministry of Higher Education for offering MyPhD scholarship to lessen my financial burden for this study. Appreciation also goes to the Ministry of Science, Technology and Innovation (MOSTI) for offering Science Fund grant to support my research experiments and conferences. My honest thanks go to my husband, Mohammad Hasbullah, my family and friends for their prayers; this dissertation is simply impossible without them. Thanks for supporting me spiritually throughout my life. Once again, I would like to express my gratefulness to everyone who has assisted and motivated me in completing my study project. Thank you to all of you.

Maizatul Akmam

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LIST OF SYMBOLS

Å	Angstrom
A	Area
A^*	Effective Richardson coefficient
a	Lattice constant, a
at%	Atomic percentage
β	Beta
c	Lattice constant, c
D	Crystallite size
D^*	Detectivity
d_{hkl}	d-spacing
e	Electron charge
h	Planck's constant
h, k, I and l	Miller indices
$h\nu$	Photon energy
I	Current
I_S	Saturation current
I_i	Illuminated current
I_p	Photocurrent
I_d	Dark current
K_B	Boltzmann's constant
k	Shape factor
m^*	Effective hole mass
m_0	Electron mass
n_{id}	Ideality factor

P_{inc}	Illumination power density
q	Electron charge
R	Reflectance
R_λ	Responsivity
S	Sensitivity
T	Temperature
$T_{(hkl)i}$	Texture coefficient
v	Speed
α	Alpha
δ	Dislocation density
γ	Gamma
α	Thermal expansion coefficient
ε	Strain
$Ø_B$	Barrier height
2θ-ω	2theta-omega
θ	Theta
θ_B	Bragg's angle
η	Internal quantum efficiency
τ_r	Rise time
τ_f	Fall time
E_g	Energy band gap
W	Work function
V_{Ga}	Gallium vacancy
V_N	Nitrogen vacancy

LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
AZO	Aluminium doped zinc oxide
BSE	Backscattered electron
CIGS	Copper indium gallium selenide
CNTS	Copper nickel tin sulfide
CZTS	Copper zinc tin sulfide
CSD	Chemical solution deposition
CVD	Chemical vapor deposition
DC	Direct current
EDX	Energy dispersive X-ray
ECR	Electron cyclotron resonance
FESEM	Field-emission scanning electron microscopy
FWHM	Full width at half maximum
f.c.c	face centered cubic
FET	Field-effect transistors
FTIR	Fourier transform infrared
h.c.p	hexagonal close packed
HVPE	Hydride vapor-phase epitaxy
IPA	Isopropyl alcohol
I-V	Current voltage
I-t	Current time
IR	Infrared
JCPDS	Joint committee on powder diffraction standards
LCD	Liquid crystal display
LED	Light emitting diode
LMBE	Laser Molecular Beam Epitaxy
LPMOCVD	Low pressure metal organic chemical vapor deposition
LO	Longitudinal-optical
MIGS	Metal induced gap states
MS	Metal semiconductor
MBE	Molecular beam epitaxy

MOCVD	Metal-organic chemical vapor deposition
MOVPE	Metalorganic Vapor Phase Epitaxy
MSM	Metal-semiconductor-metal
NBE	Near band edge
NRs	Nanorods
NWs	Nanowires
O/E	Optical to electrical
PA-MBE	Plasma assisted molecular beam epitaxy
PD	Photodetector
PVD	Physical vapor deposition
PL	Photoluminescence
PDCR	Photocurrent to dark current ratio
RF	Radio frequency
RMS	Root mean square
SAMs	Self-assembled monolayers
SBH	Schottky-barrier height
sccm	Standard cubic centimeter per minute
SE	Secondary electron
SLG	Soda lime glass
SRH	Shockley-Read-Hall
SMU	Source measure unit
SOFC	Solid oxide fuel cell
TM	Transition metal
TO	Transverse-optical
UV	Ultraviolet
UV-Vis	Ultraviolet visible
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy

LIST OF APPENDICES

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PERTUMBUHAN NANOBAHAN GALIUM NITRIDA MELALUI KAEDAH SALUTAN CELUP

ABSTRAK

Pada fasa awal, larutan pendahulu berasaskan etanol digunakan untuk mendeposit nanobahan GaN menggunakan diethanolamine (DEA) sebagai penstabil. Pertama, kami menyiasat kesan kelajuan pengeluaran pada sifat morfologi dan struktur nanobahan GaN. Dengan mengoptimumkan kelajuan pengeluaran ke 50 mm/min, spektrum XRD menunjukkan keamatan tertinggi yang mempamerkan ketegangan terendah dan saiz kristal yang paling besar antara sampel lain. Selanjutnya, kami menyiasat hubungan antara pengaruh kitaran celupan pada kualiti kristal nanobahan GaN. Kami memerhatikan kemunculan satah GaN(002) dengan menambah bilangan kitaran mencelup daripada satu kepada lapan kitaran. Kekuatan puncak GaN E_2 (tinggi) mencapai maksimum dan mengesahkan fasa wurtzite GaN untuk sampel yang didepositkan pada lapisan kelima. Seterusnya, pengaruh jumlah penstabil yang berbeza ke atas sifat morfologi nanobahan GaN telah diperiksa. Pada 0.75 ml DEA, saput terdiri daripada butiran heksagon mengandungi orientasi pertumbuhan pilihan satah GaN (002). Analisis XRD mengesahkan kualiti kristal tinggi sampel dengan nilai nisbah atom Ga:N yang tertinggi. Garis kontur Gaussian bagi mod fonon GaN E_2 (tinggi) menunjukkan saput yang dideposit pada 0.75 ml DEA secara relatifnya bebas tekanan. Larutan sol menggunakan mono-ethanolamine (MEA) dan 2-Methoxyethanol (2-ME) diperkenalkan disebabkan kebolehbasahan tinggi dan kadar penguapan yang cepat. Hal ini akan memintas kelikatan tinggi larutan DEA-Ga_2O_2 yang menggunakan ethanol dan DEA untuk mensintesis nanobahan GaN. Larutan sol yang diperkenalkan ini digunakan untuk memdeposit saput tipis β-Ga_2O_3 sebagai

lapisan transisi untuk pertumbuhan nanobahan GaN. Analisis ini memberi tumpuan kepada penyiasatan keadaan penyepuhlindapan filem nipis β-Ga_2O_3 dengan mengubah suhu penyepuhlindapan, masa dan kadar aliran gas nitrogen. Suhu dan masa penyepuhlindapan terbaik adalah 900ºC dan 60 min masing-masing dengan 300 sccm merupakan kadar alir N_2 yang ideal. Seterusnya, keadaan nitridasi yang berbeza; suhu, masa dan kadar aliran ammonia untuk penyediaan nanobahan GaN telah disiasat. Jelas sekali, penukaran Ga_2O_3 kepada GaN adalah berkesan pada 850ºC dengan penampilan fasa tunggal GaN(002) semasa 90 minit nitridasi di bawah 600 sccm kadar aliran gas ammonia. Akhirnya, MSM UV PD berasaskan GaN dengan responsiviti bernilai 0.266 A/W berfungsi pada bias voltan terendah 2V telah difabrikasi. Masa bangkit dan masa pereputan yang dilaporkan adalah 77 ms dan 80 ms masing-masing.

GROWTH OF GALLIUM NITRIDE NANOMATERIALS BY SOL-GEL DIP COATING METHOD

ABSTRACT

In the early phase, ethanol-based precursor solution was employed to synthesis GaN nanomaterials using diethaolamine as surfactant. First, we investigated the impact of varying withdrawal speeds towards morphological and structural properties of dip coated GaN nanomaterials. By optimizing withdrawal speed of 50 mm/min, the XRD spectra shows highest intensity which exhibits lowest micro strain and largest crystallite size among other samples. Further, we investigate the relationship between the impacts of varying dipping cycle towards the crystalline quality of the GaN nanomaterials. We observe the emergence of GaN(002) plane by raising the total number of dipping process from one to eight cycle. The strength of GaN E_2 (high) peak reaches its maximum and confirms the phase of wurtzite GaN for sample deposited at fifth layer. Next, the effects of varied amount of surfactant towards morphological structure of GaN nanomaterials were examined. At 0.75 ml of DEA, film consists of hexagonal grains which consist of favoured growth orientations of the GaN(002) plane. The XRD analysis confirms the high degree of crystallinity of the sample with the highest value for Ga:N atomic ratio. The GaN E_2 (high) phonon mode from Raman fitted Gaussian peak reveals that the films deposited at 0.75 ml of DEA is relatively stress free. A precursor sol utilizing mono-ethanolamine (MEA) and 2-methoxyethanol (2-ME) were proposed owing to their superior wettability and rapid rate of evaporation. This would circumvent the high viscosity of DEA-Ga_2O_2 precursor sol when using ethanol and diethanolamnine to synthesis GaN nanomaterials. This new proposed precursor sol is used for the deposition of β-Ga_2O_3 thin films as

transition layer for the growth of GaN nanomaterials. The analysis focused on the investigation of annealing parameters on β-Ga_2O_3 thin films by varying annealing temperature, time and nitrogen flow rate. The best annealing temperature and duration were 900ºC and 60 min respectively with 300 sccm being the ideal N_2 flow rate. Next, varying nitridation conditions; temperature, duration, and ammonia gas flow for the preparation of dip coated GaN nanomaterials were investigated. Seemingly, the transformation of Ga_2O_3 to GaN is successful at 850ºC with appearance of single phase GaN(002) during 90 minutes of nitridation under 600 sccm of ammonia gas flow rate. Finally, GaN MSM UV-A photodetector having responsivity value of 0.266 AW^{-1} operates at lowest bias 2V was fabricated. The reported rise and decay time were 77 and 80 miliseconds respectively.

CHAPTER 1

INTRODUCTION

1.1 Background of research works

A quite number of significant advancements in III-V nitrides have been reported in the current years. The group III-nitrides such AlN, GaN and InN are the preferred compounds for high efficiency device performance. Gallium nitride (GaN), the extremely used III-nitride alloy, has been devoted to the improvement of high potential use in numerous electronic and optoelectronic technologies owing to its remarkable performance and reliability. Gallium nitride has garnered wide array of interest as a promising synthesis element for various optoelectronic applications like sensors, blue LEDs and ultraviolet light emitting products, as well as in high efficiency solar cells owing to its large forbidden gap approximately 3.4 eV at 300K. By virtue of its wide direct band gap, GaN semiconductors with high breakdown voltage, high saturated drift velocity, high external photoluminescence quantum efficiency and high excitonic binding energy of 20 meV has drawn great interest as a potential material for solid-state lighting and displays. Due to its extreme hardness, chemical and mechanical stability, and high-power density, wurtzite GaN is a very effective semiconductor compound for fabricating optoelectronic devices such as LEDs, microwave and recently, power electronics. Blue and UV-emitting diodes, radiation-resistance electronic devices, and electronic devices operating with extreme temperature and frequency are among the applications.

Advanced epitaxial growth techniques like Molecular Beam Epitaxy, Ultra-High Vacuum Chemical Vapor Deposition and Magnetron Sputtering are normally utilised to synthesis high quality GaN films. These procedures, however, necessitate time-consuming setup tools and have a high manufacturing cost. As a result, a simple and cost-effective approach of growing GaN thin films is highly recommended. Wet chemical solution processes of thin films deposition mainly involved spray pyrolysis, spin coating and dip coating. Compared to spray and spin coating, dip coating approach makes it simple to coat a vast surface area substrate, various shapes, and coating on both sides. Furthermore, it is attainable to prepare multiple layered coatings. Sol derived films by this approach adopts a one-step and low-cost procedure that does not necessitate any complicated set-up instruments. Due to these reasons, it is imperative to do research into the sol-gel dip coating method to give experimental data for the underlying mechanisms.

Sol-gel is a facile wet chemical method widely used in the preparation of nanoparticles such as metal oxides, nitrides, or carbides. As the name implies, sol-gel is derived from two distinct words: sol- and gel. The chemical reaction involved in sol-gel synthesis is primarily hydrolysis in aqueous solutions and condensation of inorganic or metal-organic precursors. The hydrolyzed precursors are condensed together to form small colloidal nanoparticles dispersed in the precursor solution. The suspension of the colloidal particle is called sol. The particles size ranges from 0.1-1 μm in non-covalent interactions such as hydrogen bonds and van-der wall forces at which gravitational forces is neglected. During condensation, the sol nanoparticles further agglomerate, forming a continuous oxo-bridged network of polymeric-based materials [1]. An opaque substance is obtained forming a fibrous network called a ‘gel’ with significant amount of liquid in the solution mixtures. The viscosity of the suspension increases

following the evaporation of precursor until gelation occurs forming a three-dimensional network structure. In principle, dip coating essentially consists of three stages: immersion, dwell, and withdrawal for thin film deposition. Initially, a metal-organic based precursor sol is made at the first place. The substrate is first positioned vertically on the holder before being partially or completely submerged in the precursor sol bath. In order to allow for ion adsorption from the precursor to the substrate, the substrate is allowed to dwell for the designated amount of time during the immersion step. Following that, the substrate is withdrawn from the solution and allowed to evaporate until the as-deposited layer is left on the substrate. For quicker evaporation, drying can also be done on a hot plate. Lastly, a thin layer of nanostructures may form on the substrate and ready for the next annealing step.

Dip coating offers controlled homogeneity in bio ceramic coating of synthetic hydroxyapatite (HAP) for bio-medical applications especially in load-bearing implants [2]. The ability of dip coating to coat interior fibers of fabrics also facilitate the hexagonal boron nitride (*h*-BN) coating on SiC fibers of ceramics matrix composites (CMCs) [3]. Ion incorporations are effective when using dip coating in electrolytes coating of large scales solid oxide fuel cells (SOFCs) [4]. This method also been regarded as an alternative in core and cladding material coatings onto polymer optical fiber (POFs) [5], and use in BN coating as an interphase between fiber and matrix of SiCf/SiC composites [6]. This approach has also been widely used in self-cleaning superhydrophobic surfaces [7], [8] and antireflective (AR) coatings [9]. Generally, dip coating method also adopted in preparation of metal oxides; NiZnO [10], TiO_2 [11], ZnO [12], sulphides; $AgInS_2$ [13], CuS [14], CdS [15], and nitrides; BN [6], [16], GaN [17] thin films. Yet, rare fabrications on sol-gel dip coating approach for III-nitride thin films were presented especially on GaN films. Nonetheless, there are some limitations

were seen using this approach which precipitation of BN precursor residual limits the uniformity to evenly distributed the surface of impregnated fibers from conventional dip-coating method claimed by Jianggao et al [3]. Next, Wan et al reported TiO_2 intermediate products were formed at high treatment process has weakened the ability of gravity and capillary forces to cover the substrates. The elongated defects from inhomogeneous coating would induce substrate corrosion of the photoelectric and photocatalytic properties [11]. In another study carried out by Adelkhani et al, the authors seen highly branched and discrete clusters polymer films deposited under base-catalyzed precursor sol. Meanwhile, linear or randomly branched polymers were formed from acid-catalyzed based precursor. These discrepancies may influence the corrosion resistance properties of the sol–gel derived silica film [18]. In addition, selection of withdrawal speed is important especially on hydrophobic and permeable substrates when using neither aqueous nor polymer-based precursor solution. Cracking and porosity from improper withdrawal speed would cause thickness inhomogeneity that weakens chemical barrier properties of the coating and induce substrate corrosion as seen on the TiO_2 films [11]. Low withdrawal speed forms thicker wet films due to capillary forces, whereas greater withdrawal speed evaporates solutes faster due to viscous drag to correlate good surface coverage and uniformity in film thickness. The hydrolysis and condensation reaction during gel formation in the precursor sol are also influenced by pH values, which in turn affect the morphological structures of ZnO films as reported by Alias et al [19]. The author observed agglomeration of large particles in acidic to neutral pH precursor solutions due to low concentrations of OH- ions which inhibits formation of well-structured ZnO film. The pH values contributed to the change of number of ZnO nuclei in the prepared precursor sol. Typically, structural, morphological and optical properties of the sol-gel derived films are tailored according

to the variables like precursor used in, withdrawal speed and dipping cycle that define the homogeneity of the deposited film.

In conclusion, in-depth deposition and characterisation of GaN nanomaterials synthesized via sol derived dip coat would be the focus in this proposed work. The influence of dipping parameters, which include precursor concentration, withdrawal speed and quantity of dipping process on their crystallinity, morphological, and reflectance properties of synthesized GaN films will be measured. Finally, GaN-based optoelectronic device will be set up and its performance will be tested. This research will provide a thorough study on the characterizations of sol derived dip coated GaN thin films. This could lead to considerable advances in condensed matter physics.

1.2 Problem statement

The purpose of this experiment is to investigate a simple synthesis to grow good quality GaN nanomaterials adopting the sol-gel dip coated process, which is less complicated, cheaper, and safer than conventional growth methods.

Although plenty of research has been done for the sol derived dip coat approach for generating thin solid film, there has been little research on GaN nanomaterials. There are few factors affecting the GaN thin films properties using this method. Reported studies on dipping variables like rate of withdrawal speed [20]–[25], dipping cycle [12], [13], [26]–[28] and concentration of precursor solution [29]–[34] are the key factors determining the homogeneity of the film. However, the information about the compatibility of the coated material influenced by the dipping variables and synthesis mechanisms on GaN nanomaterials have not yet been fully exploited by any researchers.

However, difficulties were encountered while using this method to synthesise GaN nanomaterials. The selection for precursor solution to synthesise GaN nanomaterials for dip coating approach need to be investigated. These difficulties are due to the complexity of solution mixing and poor wettability of inherently hydrophobic surfaces like silicon when in contact with water-based precursor. Plus, the main disadvantage of precursor sol is to contain catalyser derived sol. There are reported studies using ammonium hydroxide [35], glacial acetic acid [36], citric acid [37] for preparing stable precursor solution to avoid agglomeration of solute particles due to sol ageing. In this context, non-catalysers precursor sol is of interest, and it is now necessary to pay attention to acid-free prepared sol to deposit GaN nanomaterials. However, solvent and surfactant using 2-methoxyethanol and mono-ethanolamine with gallium nitrate hydrate powder prepared for sol-gel dip coating for the GaN nanomaterials deposition has not been reported elsewhere. This precursor sol may possess ease of chemical composition and stoichiometry control with good purity due to high evaporation rate and good wettability. As a result, having a homogeneous precursor solution capable of producing high-quality GaN nanomaterials is crucial.

The GaN-based MSM configuration photodetector has emerged as a choice owing to their ease of fabrication and low dark current. Alloy GaN finds potential application in the UV detector array due to its excellent thermal stability and large bandgap. In particular, GaN materials gain considerable interest in the fabrication of MSM PDs to detect UV-A. Great efforts have been made to improve the Figure of Merit of the MSM PDs of the GaN materials by synthesizing via various methods and optimizing their nanomorphology. Surprisingly, for such a widely studied material there is rare reports in the published literature on its Figure of Merit such as sensitivity and detectivity using wet chemical solution especially dip coating method. Among the

coating method recently investigated, GaN MSM PDs have exhibited high value of ideality factor >1 and low Schottky barrier heights (SBH) [38], [39] to date using spin coating and RF sputtering respectively. Therefore, considering the stable rise of photo-response, the application of dip coating solution process that is compatible with fast processing production is one of crucial requirements for PDs application. Among various preparative methods, sol-gel dip coating has proved to be popular means of fabricating nano-morphology thin films. The main advantage of sol-gel dip coating process is the ability for large coating area on the components of complex shape with good homogeneity at relatively low processing temperature. GaN-based MSM PDs grown via sol-gel dip coting may led to tendency for continuous and simultaneously improvement in the performance of PDs.

Hence, a thorough analysis in synthesis of two-dimensional GaN nanomaterials via dip coating approach will be carried out to provide notable information for future researchers.

1.3 Research objectives

The first objective is to synthesize sol-gel dip-coated GaN nanomaterials without the use of metal or polymer catalysers using diethanolamine and ethanol as precursor sol deposited on AlN/Si(111) substrates. Plus, characterize the effects of dipping variables like withdrawal speed, number of cycles and amount of surfactants on the synthesized GaN films and study their structural, morphological and optical properties.

The second objective is to propose precursor sol without the use of metal catalysers using 2-methoxyethanol and mono-ethanolamine in deposition of β-Ga_2O_3 film as a transition layer for the GaN nanomaterials growth. Plus, optimize the influence

of annealing parameters; annealing temperature, time and annealing ambient with further investigation on the morphology, structural and optical properties of the β-Ga_2O_3 films on bare *n*-Si(100) substrates as seed layer for GaN growth.

The third objective is to deposit GaN nanomaterials from the β-Ga_2O_3 seed layer on *n*-Si(100) substrates without the help of AlN template. Plus, optimize the influence of ammonisation parameters; nitridation temperature, time and ammonia gas flow rate to achieve nanomaterials layer with high Ga:N ratio on heterojunction Si substrates for GaN-based MSM photodetector device.

The final objective is to fabricate and to evaluate the performance of GaN-based nanomaterials MSM UV-A photodetector using Pt/Ga/Si heterojunction for fast photo-response and reliable figure of merit photodetection by sol-gel dip-coated method.

1.4 Novelty of the research works

Sol-gel dip coating is widely used to synthesize oxide and sulfides nanostructures with great success. However, the synthesis of GaN nanomaterials via sol derived dip coating is uncommonly documented. The morphological, structural and optical properties of the GaN nanomaterials have yet to be extensively studied in terms of varying dipping variables like withdrawal speed, dipping cycle and precursor concentration. Noteworthy, this work employs the sol-gel dip coating technique to synthesis hexagonal wurtzite GaN(002) nanomaterials on AlN/Si(111) in varying dipping parameters and the results are repeatable and reproducible under the same conditions.

Apart from that, this work implements monoethanolamine (MEA) as surfactant that offers rapid evaporation rate and improved wettability of the precursor sol.

Although it is well known that MEA surfactants are frequently employed in the preparation of oxide films solution, the mature of MEA in the synthesis of dip coated GaN nanomaterials is unlikely been investigated. The synthesis of GaN nanomaterials using combination of MEA and 2-ME as precursor sol has proved its potential in the growth of the material via this route. To the best of the knowledge, the ammonisation of β-Ga_2O_3 transition layer on *n*-Si(100) substrates to grow GaN nanomaterials without any assistance of acid as catalyser in the precursor sol does not exist in any reported works. The influence of nitridation conditions; temperatures, time and NH_3 gas flow rate on the dip-coated β-Ga_2O_3 thin films are proposed. In addition, a novel MSM configuration of UV-A photodetector based on dip coated GaN nanomaterials was fabricated. No similar work is reported up to this point where a sol-gel dip coating approach was utilized to grow a GaN/Si heterostructure with high photo-response and detectivity using combination of MEA with 2-Me as sol precursor.

1.5 Outline of dissertation

A thorough overview of GaN growth technology from the literature is included in **Chapter 2** together with background study on the sol derived technique to synthesis GaN nanomaterials. Also discussed are the variables that influence the deposition of GaN nanomaterials grow using sol-gel approach. The fabrication of GaN-based MSM photodetectors by other literatures is also discussed in this chapter. The fundamental physical and electrical properties of GaN alloy as well as underlying mechanisms of the sol-gel process were covered in the last part. Additionally, a brief explanation of each characterization tools' operating principle and their mechanisms together with GaN-based photodetector design and working principle are also discussed.

The earliest part of **Chapter 3** elaborates about methodology of growing GaN nanomaterials using ethanol and diethanolamine as the starting precursor sol. The precursor sol is used to deposit GaN nanomaterials of varying withdrawal speed, dipping cycle and amount of surfactant on AlN/Si(111) substrates. In next section, a new precursor sol using 2-methoxyethanol and monoethanolamine is demonstrated to deposit transition layer of β-Ga_2O_3 for GaN nanomaterials on *n*-type Si(100) substrates. The annealing and nitridation parameters of growing GaN nanomaterials are explained throughout the topic. The chapter is closed with the explanation of photodetection measurements of GaN photodetector using MSM configuration. The flow chart of the study is also shown.

Chapter 4 explains the characterizations of the dip coated GaN films utilizing ethanol and diethanolamine as the precursor sol and presented in the first section of this chapter. It covers on structural and optical analyses of varying parameters of the dipping processes, i.e., withdrawal speed, number of dips coated layers and amount of surfactant. The synthesis and characterization of the dip coated GaN thin films are then discussed in the next part using the new proposed precursor sol; 2-Methoxyethanol and monoethanolamine. The investigations are conducted into two studies: annealing and nitridation conditions effects on the as-synthesized GaN nanomaterials. The films were first grown to deposit Ga_2O_3 as a transition layer and the conversion from Ga_2O_3 into GaN films were conducted under varying nitridation parameters.

Chapter 5 discusses the fabrication of GaN photodetector using the optimized sample. The performance and Figure of Merit for the fabricated device are elaborated in detail. Finally, **Chapter 6** summarized the findings and limitations of this research works. In addition, suggestions for potential further works are made.

CHAPTER 2

LITERATURE REVIEW AND THEORETICAL BACKGROUND

2.1 Introduction

The fundamentals of the GaN material are covered in the first section of this chapter, such as its crystalline properties, physical constants, and other characteristics. Next, the sol-gel dip coating deposition mechanism is described in the second half of this chapter to enable better knowledge underlying the dipping process. This chapter also covers research background, and challenges faced in preparing GaN nanostructures. A few traditional techniques used to fabricate GaN thin films such as HVPE, MOCVD and MBE were discussed along with chemical deposition method. The parameters affecting the deposition of GaN thin films via sol derived dip coating approach are also the focus in this chapter. These factors include withdrawal speed, dipping cycle and amount of surfactant, as well as annealing and nitridation conditions during the synthesis. Additionally, a review of GaN-based photodetectors employing metal-semiconductor-metal configuration deposited using various methods is reported.

2.2 An overview in fabrication of GaN nanomaterials

In the past few decades, the three most popular epitaxial techniques have been used to fabricate GaN nanostructures; primarily hydride vapor-phase epitaxy (HVPE), metalorganic chemical vapor deposition (MOCVD) and reactive molecular beam epitaxy (MBE). In 1969, Maruska and Tietjen published an early report on the manufacture of GaN fabricated using HVPE [40]. This epitaxial growth was the first to be developed more than a decade ago to deposit GaN. With the use of this technique, Kim et al. [41] were able to demonstrate free-standing GaN substrates in 1998. This

was made possible by the high deposition rate and capacity to deposit thick GaN films by this growth technique. The thick-film GaN which has current maximum size of 350 μm thickness and 10 mm^2 area successfully deposited on Al_2O_3 substrate. The Al_2O_3 substrate was then removed leaving an optically and electrically superior GaN single crystalline appropriate for the homo-epitaxial growth of GaN. Then, in 1999, Lee et al [42] attempted a similar endeavor. By incorporation of ammonia, chlorinated gallium, and nitrogen as carrier gas during a 30-minute deposition at 1125°C, the authors were able to fabricate GaN-buffer layers and ~30 μm thick GaN-films on sapphire substrates. However, nitrogen trichloride may develop when ammonia dissociates at high temperatures and begins to react with hydrochloric acid, even though HVPE has the benefit of rapid growth and the ability to generate a thick epitaxy layer.

Metalorganic chemical vapor deposition, previously called metalorganic vapor phase epitaxy (MOVPE) is one of chemical vapor deposition approaches employed to grow highly crystalline thin films. Manasevit and Simpson first demonstrated this hetero-epitaxial growth in 1969 to develop III-V compound semiconductor of gallium arsenide (GaAs). Since then, this technique has grown various new exploration interest to the leading fabrication equipment for electronic and optoelectronic semiconductor devices used in communications, high frequency detection tools, remote control, surface imaging, and lightings. Since the successful creation of the novel MOCVD system for GaN growth by Nakamura et al [43] decades ago, GaN films deposition by this technique has favoured wide array of interest. For a deposition of III-V GaN semiconductor, an alkyl organometallic trimethylgallium (TMGa) is used as the group III precursor and a hydride, NH_3 is used for the group V precursor. This method relies on the gas phase transfer of the materials to be pyrolyzed on substrate surface as thin films via surface chemical reaction. As a result, a highly crystalline, multi quantum well

heterostructures of high homogeneity thin layers of semiconductor compounds can be grown.

This approach has a substantially higher throughput than HVPE. However, while realising good-quality films and a rapid growth rate at a scale desirable for mass production, this approach has drawbacks because of the high temperatures and complex gas reaction and chemical surface reactions that result during the epitaxy process of GaN films. Although MOCVD has generated the greatest quality GaN-based devices so far, it appears that metal-organic compounds are more expensive than inorganic compounds and vast amounts of NH_3 gas are required throughout the synthesis. Plus, high deposition temperatures are typically used in HVPE and MOCVD techniques to fabricate GaN layers. The functionalities of substrate, deposited films and device performance may be adversely impacted by the generation of unwanted interface compounds or alloys because of high growth rate temperature. Conversely, a steep or abrupt contact at the hetero interface is necessary for most high-performance device applications. Thus, low growth temperature is needed to minimize the production of thick interfacial layers in this regard [44].

In addition to HVPE and MOCVD, MBE is another fabrication technique that can fabricate high-quality layers with sharp interfaces and precise control over elemental composition, thickness, and doping. During the growth process, the heated crystals that have already undergone surface processing to achieve a nearly atomically clean surface are incident by atoms or molecule beams in an environment of ultrahigh vacuum. When the impending constituent atoms come into contact with the substrate, a crystalline layer is formed, resulting in an epitaxial thin film [45]. This technique was used in 1994 by Ohtani et al [46] to grow single phase wurtzite GaN layer on Si (111)

wafers having AlN as buffer layers. The investigation of MBE growth of GaN films grown on Al_2O_3 substrates with GaN as buffer layers was later fabricated by Hughes et al [47] to be able to circumvent the issue about GaN nucleation between highly mismatched substrates. Thirumaleshwara et al [48] also adopted this vapor-phase approach to manufacture GaN thin films directly on silicon of great crystallinity utilizing plasma assisted molecular beam epitaxy (PA-MBE). The authors reported that a phase mixture encompassing both cubic (β) and hexagonal (α) modifications was found in the GaN films produced directly on the Si (100) orientations. The authors claim that nitridation of the Si surface promotes the formation of phase pure hexagonal GaN films while employing nitrogen plasma in a base vacuum.

Key issues plaguing with the current III-V nitride epitaxy by conventional MBE are the low deposition rate, which is typically 0.004-0.15 μm/hr. The anomalous effect from ion damage observed by nitrogen-plasma ECR sources and insufficient diagnostics in typical MBE systems to monitor and manage nitrogen plasma species during synthesis are the drawbacks [47]. Further, a modified MBE equipped with radio frequency (RF) plasma to mitigate lower ion content and reduce surface inhomogeneities with improved growth rate from 0.1 to 1 μm/h is proposed by Zhang et al [49]. Although polar GaN nanostructures in *c*-axis preferential growth can be realized, nonetheless this approach results in random nucleation with a significant density of point defects from the *n*-carriers. Plus, there has also been challenges to control the size, shape, position, lateral or vertical growth direction of the low-dimensional nanostructures using this route [50]. Although high-quality films can be fabricated using this vapor-phase fabrication technique, multiple issues still need to be addressed, including high production costs and cumbersome setup. Thus,

a straightforward and inexpensive alternative fabrication approach is therefore favorable.

Since low dimensional nanostructures hold the potential to develop the reliability of device operation and the detectivity of sensors, numerous strategies have been investigated to date with the purpose of synthesizing GaN. Due to these factors, substantial emphasis has been placed on the development of GaN thin films at low substrate temperatures using simpler fabrication techniques. However, high temperature and high nitrogen pressures are necessary to circumvent the large kinetic barriers for crystallization. Therefore, a straightforward and practical synthetic approach is required to produce the GaN thin films.

2.3 Preparation of nanomaterials via sol-gel dip coating method

Wet chemical methods, specifically the sol-gel approach, appear to hold promise in the search for cost-effective techniques to synthesis III-V nitride films. In comparison to the above-mentioned conventional techniques, the technique for film deposition used in the sol derived method is more distinguishable and convenient. For high-quality films to be applied to optoelectronic devices, research on the synthesis mechanisms of GaN thin films synthesized via sol derived is vital. Sol-gel coatings or more generally chemical solution deposition derived coatings are now being researched for diverse applications including ferro- and dielectrics, sensors and actuators, layered superconductors, and functional coatings. This approach exhibits simple composition control and surface uniformity is possible across a large surface area. The sol-gel process forms a thin and homogenous coating on a substrate utilizing a chemical liquid (precursor). The five primary types of coating implementing sol solution are spray coating, capillary coating, roll coating, spin coating and dip coating. Amongst range of

wet chemical thin film synthesis processes, dip coating is one of the techniques that has been practically used the longest. In 1939, Jenaer Glaswerk Schott & Gen issued their first patent for silica films derived from sol-gel which was based on this method. In 2015, a method for growing GaN thin films called sol-gel spin coat was suggested by Fong et al. [51]. This method is comparatively easier, less expensive, and safer than the traditional approaches. The success of the sol-gel approach in creating a good crystalline GaN thin film has clearly proved its promise and potency of wet chemical deposition.

The benefits of dip coating deposition include low-cost experimental setup, environmental friendliness, and ease of synthesis of high-quality thin films that can include impurity doping. This solution deposition technique is mostly utilized for uniform coating of large areas which thickness, and surface microstructures can be controlled by dipping variables. By regulating the number of dipping cycles, the layer-by-layer deposition each time the substrate was submerged in the precursor bath allows the dip coating technique to offer thin films of such excellent quality. The control over layer thickness and deposition rate by controlling the dwell time between dips and by regulating the substrate pull-out velocity are two additional benefits of dip coating. When compared to spin coating, a larger area of film can be covered by manipulating these deposition parameters.

Dip coating is widely employed in various manufacturing processes to deposit liquid film onto substrates derived from a precursor solution for such purposes as protection, magnetization, adjusting refractive index and lubrication. Dip coating has been employed extensively in synthesizing oxides films, particularly the oxides of copper [52], titanium [53], [54], nickel [55] and zinc [56], [30]. This method has also

been utilized extensively to incorporate the doping ability for transparent conducting oxides (TCOs) films, such as Al-doped ZnO [57], Ce-doped SnO_2 [58] and Mo-doped In_2O_3 [59]. Likewise, dip coating provides better coating on the copper zinc tin sulfide (CZTS) thin films [32], [60] and offers advantages for controlling the homogeneity of wide surfaces, particularly in solid oxide fuel cells (SOFCs) [4], [61].

However, it should be noted that this method has yet to be thoroughly investigated in III-nitride materials. Niesen et al [62] demonstrated an early report on GaN deposition via dip coating synthesized from a solution of the polymeric precursor based on gallium carbodiimide. According to the authors, most of the substrate surface was left uncoated whereas the structure of self-assembled monolayers (SAMs)-derived GaN films is made up of tiny pores that are randomly distributed throughout the polymer in statistically scattered patches state. Despite successful attempts to grow GaN thin films, the authors advised that more studies are required to improve the conditions for film formation. An investigation of depositing GaN thin films via dip coating approach has been made by Sinha et al [17]. The author adopted acetate derived sol precursor to grow *c*-axis oriented wurtzite GaN deposited on amorphous silica substrates without facilitating buffer layer. Different phases of gallium oxide thin films; α-GaO(OH) and (α+β)-Ga_2O_3 were nitridated under varying temperature and time. The lowest thermal stability α-GaO(OH) film was favourable to grow GaN film with less energy for conversion at 700°C within 1h. In the latter approach, Sinha et al [36] deposited *c*-oriented GaN layers on amorphous glass substrates by ammonisation of three distinct thin films of sol-gel derived α-GaO(OH), α-Ga_2O_3 or β-Ga_2O_3 synthesized on GaN buffer layer. However, the authors advise more research to be done to fully comprehend the mechanism underlying the deposition of GaN films with a *c*-plane orientation on amorphous glass substrates.

Unfortunately, there are substantial concerns when utilizing this method to synthesis GaN films since the prepared precursor adheres to hydrophobic substrates poorly, making it difficult for the sol precursor to quickly become wetted when in contact with high surface tension substrate. Therefore, studies on the formation of GaN films on silicon substrates using sol derived dip coating are scarce. Furthermore, the report of the impact of dipping variables on the crystallinity of GaN layers, i.e., varying the sol concentration, withdrawal speed, dipping cycles and dipping time are extremely rare. In fact, a few issues ought to be acknowledged to grow high quality GaN thin films applying this approach.

As per our knowledge, there are scanty theoretical and experimental findings on the synthesis of GaN thin films using the sol-gel derived dip coating approach that discuss the influence of dipping parameters and growth conditions on the film's characteristics. Thus, the synthesis of GaN thin films applying this route nonetheless remains difficult. and devoted considerable efforts are needed for the refinement of the films' crystallinity. The characteristics of sol gel prepared GaN films using dip coating route is influenced by a variety of synthesis conditions. These include withdrawal speed, dipping cycles, the choice of sol precursor used for dipping, as well as the annealing and nitridation conditions. The characteristics of the GaN films are manipulated by varying the dipping variables during the synthesis. All these parameters must be considered to produce high-quality GaN thin films. Despite a quite number of research on the growth of nanostructures grown by dip coating method have been conducted, however there were few studies on this approach for depositing nitride thin films especially on GaN.

2.3.1 Withdrawal speed

Many research works have been conducted to investigate the impact of substrate withdrawal on the growth properties of dip coated films. In theory, the thickness of the wet film layered onto the substrate grows with ascendant speed of substrate withdrawal in the case of ideal fluids [63]. Reportedly, it was discovered that the substrate's withdrawal speed can affect the thickness of the deposited films. According to Berre et al. [64], the substrate withdrawal speed, *v*, impacts the thicknesses of multi-layered phospholipid films when they are withdrawn horizontally from the solution. At *v* above 1 mm s^{-1}, viscous pull acting on the substrates affects the film deposition, and the sol pulled onto the surface evaporates quickly. This agrees with the well-known Landau-Levich model. Based on the conventional model, the film thickness generated in this model grew with increasing pull-out speed at a power of 2/3 [65]. Meanwhile, Berre et al [64] deposited multilayer phospholipid films at relatively low speeds, *v* less than $\sim 10^{-1}$ mm s^{-1}. In this investigation, at which viscous pull are neglected, solutes accumulate along the contact line between the wet film and substrate, resulting in deposition of dried film above meniscus level. The deposition is perturbed by evaporation-induced flow i.e., the evaporation regime of the Landau-Levich regime. It is said that the thickness of layered films increased with the decrease of substrate withdrawal at a power of $10 \times^{-1}$ [66].

Experimentally, the withdrawal speed of the substrates for deposition of ZnO and TiO_2 films deposited using this method were studied from 1 to 12 cm/min and 12 to 18 cm/min, respectively [20]. Consequently, the authors discovered that at low withdrawal speed, the films produced inhomogeneous results in both films formation, which may be related to the thin fluid film's contraction prior to gelation. Inevitably, increased withdrawal speed appears to offer effective thickness control for the deposited

films. Another study concerning the impact of withdrawal speed on deposited films was conducted in 2018 by Roy et al [21]. They discovered that as the substrate speed increased from 1 to 4 cm/min, the thickness of the dip coated TiO_2 layers increased due to the acceleration of gelation process at higher withdrawal speed. Moreover, S. Aydemir et al [22] reported enhanced band gap energy (E_g) of nanocrystalline Al-doped ZnO (AZO) thin films from 3.20 eV to 3.25 eV and 3.27 eV with the increase of substrate withdrawal of 20, 40 and 80 mm/min, respectively. Similar dependency was established for thickness and surface RMS of the deposited films, which increase with the increase in substrate withdrawal and match with the previously reported Landau-Levich model. In a similar research work on effect of withdrawal speed, Canci et al [23] reported significant blue shift at the absorption edge due to decreased optical transmission of the CIGS thin film as withdrawal speed increases, as well as band gap tuning by modulating the substrate withdrawal from 60 to 300 mm/min on CIGS films deposited on quartz glass. Furthermore, optical investigation of ZnO:Mn published by Zohra et al [24] verifies the claim made by Canci et al where band gap varied from 3.75 to 2.76 eV with respect to substrate withdrawal for the same doping concentration. Consistent trend of ZnO thin films properties is also shown by Aydemir et al [25] where the authors reported the surface roughness, transparency in the visible region and energy band gap are dependence of withdrawal speeds.

A conclusion that can be drawn from the literature is that withdrawal speeds significantly affect the surface structure, crystallinity, and band-gap energy of the sol-gel films. Dip coating has a significant capability to be used for massive manufacture since it is simple to apply to substrates in a variety of geometric shapes. The implementation of correct withdrawal speeds is therefore important in establishing a homogeneous coating layer and can be employed where thicker coatings are permitted.

2.3.2 Dipping cycle

The self-template process can be used to explain the deposition process of layer-by-layer films grown by the sol dip coating route. The ideal film thickness is preferred for the utilization of optoelectronic devices to provide optimal device performance. With this in mind, it is essential to know the relationship between the influence of dipping cycle on the crystallinity, morphological, and reflectivity of the dip coated GaN films.

In the literature published by Mokurala et al. [26], it was deduced that the compositional ratios of pre-annealed and sulfurized copper nickel tin sulfide (CNTS) films grown on soda lime glass (SLG) substrates changed with respect to the varying dipping cycles. The thickness of the deposited CNTS films linearly increase in relation to dipping cycle. The resulting pre-annealed films from one and two dips were Cu- and Ni-rich, and S deficient. After improving the layer of dipping cycles from four to five layers, the desired stoichiometric ratio and suitable thickness of ~1-1.5 μm of CNTS films are obtained. This shows that the method being employed prevents any film from being re-dissolved into the solution. The sulfurized films of CNTS films show comparable tendencies as well. The optical bandgap and resistivity of the films are affected by the variations in the atomic percentage ratio of the films as the layer of dip increased. However, the change of elemental composition with the increase of dipping cycles is not fully understood by the authors. Hence, more experimental research is being conducted to comprehend the mechanism of elemental composition variation. Kumbhar et al [27] reported similar results of increasing intensity of preferred orientation along (101) plane when dipping cycles of dip coated TiO_2 films increase from six to eight layer. This is because as the dipping cycles rise, the thickness of the film also grows which is explained by an expansion in grain size. The reliance of

morphology on multiple dipping cycles can also be seen in the growth of spherical granular of TiO_2 films in the development of an interlink channel for current flow, which contributes to the effectiveness of the fabricated photodetector. The maximum photocurrent and responsivity of 0.64 μA and 2.15 A/W respectively at 5V bias is obtained under UV light source of 365 nm for film grown with 8 layers of dipping.

Apart from that, Huang et al. [13] reported on polycrystalline $AgInS_2$ dip-coated films grown on ITO coated glass employing varying dipping cycles from one to five layers. They discovered that the electrical characteristics of $AgInS_2$ films can be altered by altering the thickness during the dipping cycle. The researchers discovered that three dipping cycles result in a sufficient thickness of roughly ~1.53 μm for superior photo-electrochemical performance with a maximum current density of 3.50 mA/cm^2 operates at 0.5V bias voltage. It is relatively better than that of sample at five dipped cycles with ~1.00 mA/cm^2 following the same deposition. Additionally, the surface nanostructures of $AgInS_2$ films appear to be slightly altered by the dipping process, resulting in a denser and more uniform fibre-like structural morphology. However, absorption transmittance analysis for $AgInS_2$ films demonstrated that the direct band gap in deposited films was not affected by dipping cycles. This work agrees to the finding published by Xua et al [12]. According to the authors, the transmittance of ZnO dip-coated films deposited on glass substrates is slightly affected by the dipping cycle, and the averages are all above 80% in the visible wavelength. The ZnO films prepared by dip-coating with dipping cycle ranging from 3 to 12, show increasing preferred orientation (002) as the number of cycles increases, while micro strain decreases. However, they discovered that as the dipping cycles increases, the index of refraction of ZnO films improves. A transformation of microstructure from vertical to lateral growth is also investigated between 9 to 12 cycles. Meanwhile, Toubane et al. [28]

observed an increase in micro strain in dip coated ZnO nanorods with increasing of dipping cycle. The crystallinity of preferentially oriented (002) plane of ZnO nanorods is dipping cycle dependent which the crystallinity improves with increasing film thickness. Clearly, the intensity of preferential orientation increases pertaining to the increase of dipping cycles.

2.3.3 Concentration of precursor solution

Generally, the amount of surfactant significantly affects and improves the properties of deposited thin films via sol-gel dip coating technique. The effects of molarity of precursor of sol-gel derived ZnO films on its properties is discussed by Sharul et al. [29]. Various solution concentrations ranging from 0.3 M to 0.7 M were investigated in this experiment. Higher precursor molarity results in larger grains, as quantified by the lateral feature and RMS surface roughness, which increase in relation to increasing solution molarity. At 0.7 M, where transmission is at its peak, 80% of the signal is transmitted. In contrast, Thongsuriwong et al [30] observed decreasing transmittances of ZnO films as sol concentrations increased from 0.3 M to 0.1 M. The 0.1 M ZnO film comprises of microscopic ZnO granules and has the largest surface roughness, which explains the highest transparency. The reduction in transmittance thus enhanced its photocatalytic activities of the ZnO films deposited via sol-gel dip coating.

In a comparable approach, Selman et al. [31] analyse the influence of sol concentration; i.e. 2, 3, 4, and 5 mM on rutile titanium dioxide, TiO_2 nanorods. According to their experimental findings, TiO_2 nanorods deposited at 4 mM of concentration had the greatest texture coefficient, $T(_{hkl})_i$ value on the preferred plane and the least residual stress. The optimal concentration of 4 mM, also exhibits high TiO_2 density and PL UV intensity values with few defects, leading to high sensitivity of 44.4,

high gain of 1.45 and a good responsivity of 70 mA/W of TiO_2 NRs MSM photodetector. In addition, Chaudhari et al. [67] examined the incorporation of Triethanolamine (TEA) with different molarity on the production of Copper Zinc Tin Sulfide (CZTS) film. The authors discovered the existence SnS as secondary phases which exist with addition amount of 30 µl TEA. The emergence of novel secondary phases like Cu_2SnS_3, ZnS, and SnS of CZTS films is aided by increasing the amount of TEA to 150 µl and 300 µl. This is strongly corroborated by the enhanced film uniformity and CZTS stoichiometry when small amount of TEA was added. However, at greater TEA molar ratios, more porous and non-stoichiometric morphology is seen. An intriguing study on the results of varying sol gel concentration on In_2O_3 thin films is published by Yahia et al [33]. The authors noticed an emergence of new plane orientation corresponding to (321) plane by varying sol gel concentration from 0.05 to 0.25 M. According to their claims, the stoichiometric ratio of the In_2O_3 films changes in relation to precursor concentration. It is also agreed upon that the films exhibit smaller crystallite size, narrowing of the bandgap and decreased intensity of the FTIR spectrum at higher sol concentrations of 0.25M due to the deterioration of the crystal state at high molarity. In another study reported by Shakeri et al. [34], the deposition of thick film lead zirconate titanate (PZT) was varied under different molar ratios of diethanolamine (DEA) and water in the acetic acid alkoxides-based sol. The appearance of mixed phases consisting of pyrochlore (P_r) and perovskite (P_v) phases were seen on the film surface with the absence of DEA. The porosity signifies the Pb deficiency in the coating film. Further addition of DEA from 0.25 to 0.5 molar ratios shows increased crystallinity, reduced lattice distortion and well-grown grains with non-detectable pyrochlore phase in the PZT layers. Thus, it shows that homogeneity distribution is influenced by the addition of additives in the acetic acid and DEA complexations.