Linköping Studies in Science and Technology
Dissertations No. 1654

CVD solutions for new directions in SiC and GaN epitaxy

Xun Li

李珣

Linköping University
INSTITUTE OF TECHNOLOGY

Semiconductor Materials Division
Department of Physics, Chemistry and Biology (IFM)
Linköping University
SE-581 83 Linköping, Sweden

Linköping 2015

© Xun Li 2015, unless otherwise stated

ISSN: 0345-7524

ISBN: 978-91-7519-084-6

Printed by LiU-Tryck, Linköping, Sweden 2015

Table of Contents

Abstract	3
Populärvetenskaplig sammanfattning	5
Preface	9
List of papers included in the thesis	10
List of publications not included in the thesis	11
Acknowledgements	12
Part I: Introduction	13
1. Silicon Carbide	15
1.1 Physical properties	16
1.2 Crystal structure	17
2. Gallium Nitride	19
2.1 Crystal structure	20
2.2 Polarization	21
3. Chemical Vapor Deposition	23
3.1 Basic principle	23
3.2 Reactor	26
3.3 Epitaxial growth	28
4. Characterization	33
4.1 Optical microscopy	33
4.2 Atomic force microscopy	34
4.3 Photoluminescence	36
4.4 Cathodoluminescence	38
4.5 X-ray diffraction	39
4.6 Secondary ion mass spectrometry	40
5. Summary of papers	41
6. My contribution to the papers	43
7. Reference	44
Part II: Papers	51

Abstract

This thesis aims to develop a chemical vapor deposition (CVD) process for the new directions in both silicon carbon (SiC) and gallium nitride (GaN) epitaxial growth. The properties of the grown epitaxial layers are investigated in detail in order to have a deep understanding.

SiC is a promising wide band gap semiconductor material which could be utilized for fabricating high-power and high-frequency devices. 3C-SiC is the only polytype with a cubic structure and has superior physical properties over other common SiC polytypes, such as high hole/electron mobility and low interface trap density with oxide. Due to lack of commercial native substrates, 3C-SiC is mainly grown on the cheap silicon (Si) substrates. However, there's a large mismatch in both lattice constants and thermal expansion coefficients leading to a high density of defects in the epitaxial layers. In paper 1, the new CVD solution for growing high quality double-position-boundaries free 3C-SiC using on-axis 4H-SiC substrates is presented. Reproducible growth parameters, including temperature, C/Si ratio, ramp-up condition, Si/H₂ ratio, N₂ addition and pressure, are covered in this study.

GaN is another attractive wide band gap semiconductor for power devices and optoelectronic applications. In the GaN-based transistors, carbon is often exploited to dope the buffer layer to be semi-insulating in order to isolate the device active region from the substrate. The conventional way is to use the carbon atoms on the gallium precursor and control the incorporation by tuning the process parameters, e.g. temperature, pressure. However, there's a risk of obtaining bad morphology and thickness uniformity if the CVD process is not operated in an optimal condition. In addition, carbon source from the graphite insulation and improper coated graphite susceptor may also contribute to the

doping in a CVD reactor, which is very difficult to be controlled in a reproducible way. Therefore, in paper 2, intentional carbon doping of (0001) GaN using six hydrocarbon precursors, i.e. methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), propane (C_3H_8), iso-butane ($\text{i-C}_4\text{H}_{10}$) and trimethylamine ($\text{N}(\text{CH}_3)_3$), have been explored. In paper 3, propane is chosen for carbon doping when growing the high electron mobility transistor (HEMT) structure on a quarter of 3-inch 4H-SiC wafer. The quality of epitaxial layer and fabricated devices is evaluated. In paper 4, the behaviour of carbon doping using carbon atoms from the gallium precursor, trimethylgallium ($\text{Ga}(\text{CH}_3)_3$), is explained by thermochemical and quantum chemical modelling and compared with the experimental results.

GaN is commonly grown on foreign substrates, such as sapphire (Al_2O_3), Si and SiC, resulting in high stress and high threading dislocation densities. Hence, bulk GaN substrates are preferred for epitaxy. In paper 5, the morphological, structural and luminescence properties of GaN epitaxial layers grown on N-face free-standing GaN substrates are studied since the N-face GaN has advantageous characteristics compared to the Ga-face GaN. In paper 6, time-resolved photoluminescence (TRPL) technique is used to study the properties of AlGaIn/GaN epitaxial layers grown on both Ga-face and N-face free-standing GaN substrates. A PL line located at ~ 3.41 eV is only emerged on the sample grown on the Ga-face substrate, which is suggested to associate with two-dimensional electron gas (2DEG) emission.

Populärvetenskaplig sammanfattning

Denna avhandling syftar till att utveckla metoder för att syntetisera epitaxiella skikt av kiselkarbid (SiC) och galliumnitrid (GaN) med en metod som kallas chemical vapour deposition (CVD). På svenska skulle man kunna säga kemisk ångdeponering, men det gör man i praktiken aldrig utan nöjer sig med förkortningen CVD. I CVD används flyktiga källmolekyler innehållande de atomer man behöver för att bygga upp materialet – för SiC använd en molekyl innehållande kol och en innehållande kisel. Dessa molekyler späds ut i en bärgas och gasblandningen leds in i en varm kammare där gaserna reagerar med varandra och bildar materialet på ytan på ett substrat som man har lagt in i kammaren. SiC och GaN är båda material med spännande elektroniska egenskaper som kan användas för att skapa nya och bättre elektroniska komponenter. Mera precist studerar avhandlingen nya CVD-lösningar för nya inriktningar inom SiC- och GaN-teknologi.

SiC är ett elektronikmaterial med ett stort bandgap som kan användas för att göra bättre kraftkomponenter och högfrekvenselektronik. Det finns en form av SiC med ett kubiskt kristallgitter, kallad 3C-SiC, som är väldigt intressant. Detta eftersom laddningsbärare har väldigt lätt att röra sig i kubisk SiC och om man oxiderar ytan på kubisk SiC bildas väldigt lite defekter i gränssnittet mellan en oxid och SiC. Men är det väldigt svårt att göra stora kristaller av 3C-SiC som man kan använda som substrat för epitaxiella skikt, därför brukar man använda kiselsubstrat när man ska syntetisera epitaxiella skikt av 3C-SiC. Problemet man då ställs inför är att det är stora skillnader i både termisk utvidgning och gitterkantlängd mellan kisel och 3C-SiC vilket ger mängder med defekter i materialet. I avhandlingen studeras därför hur substrat av hexagonal SiC kan användas för epitaxiella skikt av kubisk SiC och hur man kan styra CVD processen till att syntetisera kubisk SiC med väldigt lite defekter i materialet.

GaN är ett annat elektronikmaterial som också har ett stort bandgap och kan användas för att göra bättre kraftelektronik och högfrekvenskomponenter. För att göra GaN-baserade transistorer dopar man ofta en del av transistorstrukturen med kol för att få ett semiisolerande skikt mellan den aktiva regionen och substratet. Vanligen utnyttjar man då kolet i de källmolekyler man använder för GaN – vanligen använder man trimetylgallium, $\text{Ga}(\text{CH}_3)_3$ – och justerar olika CVD-parametrar som temperatur och tryck för att med viss precision styra mängden kol i GaN-lagret. Man inser lätt att det finns en risk att man på detta sätt syntetiserar GaN-skikt under förhållanden långt från de förhållanden som krävs för att få optimala materialegenskaper. Därför har avhandlingen också studerat tillsats av kolkällmolekyler för att avsiktligt tillföra mer kol till CVD-processen: Tillsats av metan (CH_4), eten (C_2H_4), acetylen (C_2H_2), propan (C_3H_8), isobutan ($i\text{-C}_4\text{H}_{10}$) och trimetylamin ($\text{N}(\text{CH}_3)_3$) studerades. Vidare har avhandlingen även utnyttjat propan för att avsiktligt koldopa det semiisolerande lagret i en högelektronmobilitets transistorstruktur av GaN, denna struktur har sedan processats till färdiga komponenter vilka har testats och jämförts med konventionellt koldopade stukturer där kolet från galliumkällmolekylen utnyttjades för koldopningen. För att skapa en bättre förståelse för hur kol från galliumkällmolekylerna inkorporeras i GaN har avhandlingen också använt en kombination av termodynamisk modellering av gasfaskemi och kvantmekanisk modellering av ytkemi i GaN CVD samt experimentella resultat från GaN CVD för att ta fram en förbättrad modell för hur kol från $\text{Ga}(\text{CH}_3)_3$ inkorporeras i GaN.

Vanligen använder man substrat av safir (Al_2O_3), Si eller SiC när man syntetiserar epitaxiella GaN-lager, detta leder till stress och defekter i materialet eftersom kristallstrukturen för GaN inte riktigt passar på kristallstrukturerna för safir, Si och SiC. Nyligen har dock GaN substrat börjat bli tillgängliga och i avhandlingens sista del har effekterna av homoepitaxi – ett epitaxiellt GaN-lager

på ett GaN-substrat – studerats, både med avseende på materialegenskaperna i GaN-lagret och med avseende på egenskaper hos gränssnittet mellan substratet och det epitaxiella lagret.

Preface

This dissertation is based on my PhD study carried out between March 2011 and April 2015 in the Semiconductor Materials Division of Linköping University. The research was financed by Swedish Energy Agency, Swedish Research Council (VR), Swedish Foundation for Strategic Research (SSF) and Swedish Defence Materiel Administration (FMV). In addition, scholarship from Ångpanneföreningens Forskningsstiftelse (14-219) and Ericsson's Research Foundation (FOSTIFT-12:036) has covered most of the conference expenses.

List of papers included in the thesis

1. Double-Position-Boundaries Free 3C-SiC Epitaxial Layers Grown on On-Axis 4H-SiC
Xun Li, Henrik Jacobson, Alexandre Boulle, Didier Chaussende, and Anne Henry
ECS Journal of Solid State Science and Technology, 3 (4) (2014) P75-P81.
2. Precursors for carbon doping of GaN in chemical vapor deposition
Xun Li, Örjan Danielsson, Henrik Pedersen, Erik Janzén, and Urban Forsberg
Journal of Vacuum Science and Technology B, 33 (2) (2015) 021208.
3. Intentionally carbon doped GaN buffer layer for HEMT application: growth and device results
Xun Li, Johan Bergsten, Daniel Nilsson, Örjan Danielsson, Henrik Pedersen, Niklas Rorsman, Erik Janzén, and Urban Forsberg
In manuscript.
4. A model for carbon incorporation from trimethyl gallium in chemical vapor deposition of gallium nitride
Örjan Danielsson, **Xun Li**, Lars Ojamäe, Erik Janzén, Henrik Pedersen, and Urban Forsberg
In manuscript.
5. Properties of GaN layers grown on N-face free-standing GaN substrates
Xun Li, Carl Hemmingsson, Urban Forsberg, Erik Janzén, and Galia Pozina
Journal of Crystal growth, 413 (2015) 81–85.
6. Optical properties of AlGaIn/GaN epitaxial layers grown on free-standing Ga-face and N-face GaN substrates
Xun Li, Carl Hemmingsson, Urban Forsberg, Erik Janzén, and Galia Pozina
In manuscript.

List of publications not included in the thesis

1. Homo-epitaxial growth on low-angle off cut 4H-SiC substrate
Xun Li, Erik Janzén, and Anne Henry
Materials Science Forum, 778-780 (2014) 131-134.
2. Surface preparation of 4° off-axis 4H-SiC substrate for epitaxial growth
Xun Li, Jawad ul Hassan, Olof Kordina, Erik Janzén, and Anne Henry
Materials Science Forum, 740-742 (2013) 225-228.
3. 3C-SiC heteroepitaxy on hexagonal SiC substrates
Anne Henry, **Xun Li**, Henrik Jacobson, Sven Andersson, Alexandre Boulle, Didier Chaussende, and Erik Janzén
Materials Science Forum 740-742 (2013) 257-262.
4. Structural investigation of heteroepitaxial 3C-SiC grown on 4H-SiC substrates
Henrik Jacobson, **Xun Li**, Erik Janzén, and Anne Henry
Materials Science Forum, 740-742 (2013) 319-322.
5. CVD Heteroepitaxial Growth of 3C-SiC on 4H-SiC (0001) Substrates
Xun Li, Stefano Leone, Sven Andersson, Olof Kordina, Anne Henry, and Erik Janzén
Materials Science Forum, 717-720 (2012) 189-192.
6. CVD growth of 3C-SiC on 4H-SiC substrate
Anne Henry, **Xun Li**, Stefano Leone, Olof Kordina, and Erik Janzén
Materials Science Forum, 711 (2012) 16-21.
7. Epitaxial growth on on-axis substrates
Anne Henry, Stefano Leone, **Xun Li**, Jawad Hassan, Olof Kordina, Peder Bergman, and Erik Janzén
Silicon Carbon Epitaxy, (2012) 97-119, ISBN: 978-81-308-0500-9.

Acknowledgements

I would like to thank:

First of all, Prof. Erik Janzén and Prof. Anne Henry for giving me the opportunity to start my PhD study and also for financial and scientific support.

Dr. Urban Forsberg, Dr. Henrik Pedersen, Dr. Örjan Danielsson, Dr. Galia Pozina, Sven Andersson, Dr. Ivan Ivanov, Dr. Carl Hemmingsson, Dr. Stefano Leone, Dr. Henrik Jacobson, Dr. Didier Chaussende, Dr. Alexandre Boulle, Prof. Lars Ojamäe, Dr. Olof Kordina, Dr. Niklas Rorsman, Dr. Anelia Kakanakova-Georgieva, Dr. David Lawrence, Dr. Jordi Altimiras, Dr. Mikhail Chubarov, Dr. Mengyao Xie, Dr. Ildiko Farkas, Thomas Lingefelt, Dr. Fredrik Eriksson, Dr. Chun-Xia Du, Dr. Jianwu Sun, Prof. Nguyen Tien Son and Prof. Bo Monemar for help.

Prof. Per-Olof Holtz for following my progress of PhD study as a director of both *Agora Materiae* graduation school and IFM graduate studies.

Prof. Leif Johansson and Prof. Magnus Johansson for arranging my teaching work; Eva Wibom for helping of administration work.

The PhD colleagues of these years, Tran Thien Duc, Ian Booker, Xuan Thang Trinh, Pontus Stenberg, Björn Lundqvist, Valdas Jokubavicius, Dr. Daniel Nilsson, Martin Eriksson, Chao Xia, Chamseddine Bouhafs, Dr. Chih-Wei Hsu, Robin Karhu, Pitsiri Sukkaew, Dr. Zheng Tang and Dr. Zaifei Ma, for having a good time together.

Finally and most importantly, my parents for everything.

Part I: Introduction

1 Silicon Carbide

In 1824, the Swedish scientist in chemistry J. J. Berzelius reported on a compound with a direct silicon and carbon bond [1]. It's considered to be the first report on Silicon Carbide (SiC) in literature. In 1892, Acheson process was invented to grow SiC crystal by heating the mixture of silica (SiO_2), coke (C), corundum (Al_2O_3), salt (NaCl) and saw dust up to around 2700 °C [2, 3]. At that time, its quality is just good enough for the application in polishing and grinding. In 1906, the first SiC solid-state diode used as a detector was patented by H. H. C. Dunwoody [4]. Then only one year later, in 1907, the electroluminescence property of SiC was observed by H. J. Round [5]. In 1955, Lely technique was developed, which open the possibility to grow bulk SiC with a larger size and a better crystal quality [6]. However, the quality of that time still couldn't reach the requirements for fabricating electronic devices in industry. Therefore, with the increasing interest for silicon in the 1960s and 1970s, the research for SiC material was slowed down. Until in 1978, the seeded sublimation growth method, which could also be termed as physical vapor transport (PVT), was established based upon the Lely process. This technique further improved the bulk SiC quality and made it becomes attractive again [7, 8]. Single crystalline 3C-SiC grown on a silicon wafer was first presented in 1981 [9]. Cree Research Inc., which was founded in 1987, first commercialized the single crystalline SiC wafer grown by improved PVT process, which is suitable for the semiconductor industry [10]. In the late 1990s, wafers with higher purity produced by the high-temperature chemical vapor deposition (HTCVD) method are available on the market [11, 12]. Nowadays, high-quality SiC wafers with diameter size up to 150 mm could be purchased [13].

1.1 Physical properties

At the early days, SiC was mainly used for abrasive and cutting due to its hardness. Afterwards, with the discovery of electronic and optical properties, SiC turns out to be a promising indirect wide band gap semiconductor material. For instance, SiC has a high saturated electron drift velocity, a high electric breakdown field and a good thermal conductivity. These properties made SiC a suitable material for fabricating high-power, high-frequency, high-temperature devices. It's worth mentioning that different SiC polytypes present distinctive physical properties. 3C-SiC, for example, has higher electron mobility, better saturated electron drift velocity and reduced interface trap density with oxide [14] compared to the other polytypes. Diamond has superior properties over other indirect band gap semiconductor materials shown in table 1. However, single crystalline diamond growth technique is still at research stage, while SiC substrates are already commercialized. In addition, the dopants for both n (i.e. phosphorous doped) and p (i.e. boron doped) type diamond could not be completely activated at room temperature [15].

Table 1 Physical properties of common indirect band gap semiconductors [16-21].

Semiconductor	Diamond	Si	3C-SiC	4H-SiC	6H-SiC
E_g (eV)	5.45	1.11	2.23	3.26	3.02
μ_n (cm ² V ⁻¹ s ⁻¹)	2200	1350	1000	900	450
E_B (MV cm ⁻¹)	10	0.2	1.2	2-3	2.1
v_{sat} (cm s ⁻¹)	2.7×10^7	1×10^7	2.7×10^7	2×10^7	2×10^7
κ (W cm ⁻¹ K ⁻¹)	22	1.5	5.0	4.9	4.9
T_w (K)	2100	410	840	1230	1200

Note: E_g – band gap at 300 K, μ_n – electron mobility at 300 K, E_B – electric breakdown field, v_{sat} – saturated electron drift velocity, κ – thermal conductivity, T_w – maximum operation temperature.

1.2 Crystal structure

SiC is known to have more than 250 polytypes in existence [22], which only differ in the stacking order of tetrahedrally bonded Si-C double layers. Among them, 3C-SiC, 4H-SiC and 6H-SiC are the most common studied polytypes. The number (i.e. 3, 4 or 6) represents how many double layers needed for periodicity in the stacking sequence, while the capital letter (i.e. C or H) denotes the crystal symmetry [23]. C, H and R indicate the cubic, hexagonal and rhombohedral system, respectively. The 3C-SiC (also called β -SiC) is the only polytype with a cubic structure. Its stacking sequence could be ABC... or ACB... (Fig. 1.1a and Fig. 1.2). These two stacking sequences with a 60° rotation difference are the origin of the double position boundary (DPB), which is a common defect when growing 3C-SiC on the basal plane of 4H-SiC and 6H-SiC substrates [24]. The elimination of DPB defects is studied in paper 1. The 4H-SiC and 6H-SiC (Except β -SiC, all the other polytypes are called α -SiC.) polytypes have the stacking sequence of ABCB... and ABCACB... (Fig. 1.1b and Fig. 1.1c), with the hexagonality of 50% and 33%, respectively.

Figure 1.1 Plots of Si (white) and C (black) atoms' arrangements in (110) plane for (a) 3C-SiC and (11-20) plane for (b) 4H-SiC and (c) 6H-SiC polytypes, respectively. The position of the double layers is denoted as A, B and C. Reproduced from ref. [16].

Figure 1.2 Schematic illustration of DPB formation when growing the 3C-SiC epitaxial layer on the 4H-SiC substrate.

2 Gallium Nitride

Gallium Nitride (GaN) is a direct wide band gap semiconductor material with many attractive properties. For instance, its band gap energy is 3.4 eV at 300 K [25]. Its electron mobility is around $1350 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 300 K and $19200 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 77 K [26]. It has good thermal conductivity, which is $2.1 \text{ Wcm}^{-1}\text{K}^{-1}$ at 300 K [27]. Its breakdown field is also relatively high. The abovementioned properties enable GaN to become a promising material in many applications. After engineering the band gap of GaN with the aluminium and indium alloys, it's possible to make optical devices, e.g. light-emitting diode and photodetector [28-31], covering a long range of wavelength. GaN is also a good candidate for fabricating high-power, high-frequency and high-temperature electronics, such as heterojunction bipolar transistors (HBT), heterostructure field effect transistors (BJT), high electron mobility transistors (HEMT), heterostructure field effect transistors (HFET), metal oxide semiconductor field effect transistors (MOSFET), Schottky and p-i-n rectifiers [32].

GaN has a shorter history compared to SiC. The first report of this material, which was formed by the reaction between metallic gallium and gaseous ammonia, was published in 1932 [33]. The first growth of single crystalline GaN was reported in 1969 using halide vapor phase epitaxy (HVPE) technique [34]. The first observation of electroluminescence (blue light) in Zn-doped GaN was published in 1971 [35]. However, it's not until the problem of p-type doping has been solved [36] and poor crystal quality has been further improved that GaN material triggered the intensive research interest, so that GaN-based devices could be commercialized. It's also worth mentioning that, in 2014, I. Akasaki, H. Amano and S. Nakamura shared the Nobel Prize in Physics "*for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources*" [37], which indicates a big step in GaN history.

2.1 Crystal structure

GaN crystal is built up by Ga and N atomic bonds, which are sp^3 -hybridised. There are three polytypes being discovered so far: wurtzite (hexagonal phase), zinc blende (cubic phase) and rock salt structures [38]. Among them, only the wurtzite structure (2H-GaN) is thermodynamically stable, whereas the zinc blende (3C-GaN) and the rock salt polytypes are metastable [39, 40]. It has been reported that the stabilized zinc blende GaN epitaxial layers could be obtained by using cubic (001) substrates [41] while few studies were carried out on the rock salt structure. This thesis only focuses on the most common wurtzite GaN polytype.

The crystal structure of wurtzite GaN is shown in Fig. 2.1. This structure can be seen as two hexagonal close-packed lattices interpenetrating each other by an offset of $3c/8$. It is often characterized by lattice constants a and c . In the ideal case, $c/a \approx 1.633$.

Figure 2.1 Crystal structure of wurtzite GaN.

2.2 Polarization

Wurtzite GaN has no inversion symmetry along the c -axis. In other words, it has two faces (polarities), i.e. Ga-face ($[0001]$ direction) and N-face ($[000\bar{1}]$ direction), with different properties. This is because the shared electrons between Ga-N bonds are unequally distributed. The Ga atom is partially positive while the N atom is partially negative. This induces the distortion of GaN crystal lattice. So in reality, the c/a ratio is not the same as the ideal values [42]. This phenomenon is called spontaneous polarization. Piezoelectric polarization, which is caused by the strain, is the other commonly existing polarization in hetero-epitaxially grown GaN films. Both the spontaneous polarization and piezoelectric polarization will together cause an electric field and a sheet carrier density, which may significantly influence the final optoelectronic device performance. For instance, the spontaneous polarization should be suppressed in GaN-based LED in order to increase the hole injection rate and consequently enhancing the efficiency of light emission [43]. However, the polarization is a necessity for AlGaIn/GaN HEMTs or HFETs for the generation of the two-dimensional electron gas (2DEG) [44, 45]. Figure 2.2 shows the typical conduction band diagram of the Ga-polar AlGaIn/GaN structure. The 2DEG is positioned in the triangular region.

Figure 2.2 Schematic conduction band diagram of the Ga-polar AlGaN/GaN structure. Reproduced from ref. [46].

3 Chemical Vapor Deposition

Chemical vapor deposition (CVD), in general, is a method to deposit a thin solid film through the chemical reactions of precursors in the vapor phase. It has been widely used for the growth of semiconductor materials with device quality [47].

3.1 Basic principle

The fundamental steps involve in CVD are listed as follows (Fig. 3.1) [48]:

1. Evaporation and transport of precursors to the deposition area.
2. Gas phase reactions – intermediates and by-products are generated.
3. Mass transport of reactants to the substrate surface.
4. Adsorption of reactants on the surface.
5. Surface diffusion, nucleation and surface chemical reactions resulting the growth.
6. Desorption and mass transport of volatile by-products.

Figure 3.1 Illustration of precursor transport and reaction processes in CVD. Reproduced from Ref. [48].

There are generally three growth regimes in CVD according to the dependence of growth rate on process temperature (Fig. 3.2):

1. Kinetic limited regime. When the temperature is low, the growth rate is limited by the kinetics of either gas phase or surface reactions. In this regime, the growth rate rises exponentially with increasing of temperature.
2. Mass transport limited regime. The growth rate is almost independent of the process temperature.
3. Thermodynamics limited regime. The growth rate starts to decrease as the temperature further increases. The possible reasons could be enhanced desorption and parasitic reactions.

Figure 3.2 Growth regimes in CVD. Reproduced from Ref. [48].

Three growth modes may take place during the deposition process (Fig. 3.3):

1. Frank-Van der Merwe (layer by layer) growth mode. It happens when the absorbed atoms bond stronger to the substrate than the other atoms.
2. Volmer-Weber (three-dimensional island) growth mode. The bonding energy between atoms is much larger than that between atoms and substrate.
3. Stranski-Krastanov (layer and island) growth mode. It's a combination of Frank-Van der Merwe and Volmer-Weber growth modes.

Figure 3.3 Schematic illustration of growth modes: (a) Frank-Van der Merwe mode (layer by layer growth), (b) Stranski-Krastanov mode (layer and island growth), (c) Volmer-Weber mode (island growth). Reproduced from Ref. [49].

3.2 Reactor

Figure 3.4 Simplified drawing of a hot-wall CVD reactor configuration.

A thermal CVD reactor basically contains four parts, including precursors, gas system, a growth cell and an exhaust system (Fig. 3.4) [48].

Precursors should fulfil several requirements. First and most important, the volatility of the precursors should be sufficient enough in order to transfer to the reaction zone, and it also has an influence on the growth rate. The precursors should have sufficient temperature range between evaporation and decomposition. The precursors are preferred to have high chemical purity and low toxicity. Good thermal stability is another important factor for the precursors. For 3C-SiC growth, propane (C_3H_8) gas and silane (SiH_4) gas are used as carbon and silicon precursors, respectively. For growth of GaN, trimethylgallium (TMGa) and ammonia (NH_3) gas are used as gallium and nitrogen precursors, respectively. Propane, silane and ammonia are normally

stored in the gas bottles. TMGa is a metalorganic precursor stored in a bubbler and needs carrier gas (e.g. hydrogen) to help deliver.

The gas system is used to deliver and precisely control of the precursors to the growth cell. It's mainly composed of mass flow controllers (MFC), electronic pressure controllers (EPC), valves, filters, purifiers and stainless steel tubes.

The growth cell could have different configurations, which might be categorized as a planetary system, a close-coupled shower head system, a turbo disc system and a cold wall, hot wall or warm wall system [48, 50, 51]. In this thesis, a horizontal hot wall reactor is used. The whole susceptor, including ceiling, walls and bottom part, is surrounded by insulation materials and inductively heated by a radio-frequency (RF) coil. The sample could be placed in a different position, and in some cases a gas foil rotation (GFR) is used in order to improve the uniformity. Linköping University is the first to develop horizontal hot wall reactor for the growth of SiC [52-54]. It is because this type of reactor has better temperature profile and higher cracking efficiency of the precursors compared to the cold wall type [55, 56].

The exhaust system is utilized to remove and handle the waste (by-products, unreacted precursors). It mainly consists of vacuum pumps, particle filters and scrubbers. The vacuum pumps used in our reactor are process pump and turbo molecular pump. Scrubbers could be several types depending on the purpose, such as a burner, a dry scrubber and a water bath with acid or base.

3.3 Epitaxial growth

This term *Epitaxy* originates from the Greek root words *epi* and *taxis*, which could be translated to above and an ordered behaviour, respectively. Therefore, epitaxial growth means an ordered growth on top of the substrate. Epitaxial growth is one of the initial, and of vital importance, steps in semiconductor electronics industry. Device structure with desired parameters, such as thickness, doping level and conductivity, could be accurately obtained through this step.

The aspect of 3C-SiC epitaxy

As described below, high-quality single crystalline 3C-SiC is generally very different to be grown, which made it even be named as “the forgotten polytype” once in the history [57]. However, due to the attractive properties of both the epitaxial layers themselves and utilization as seeds for group III Nitrides and graphene [58-60], research on 3C-SiC has never been given up in semiconductor community. 3C-SiC epitaxial layers have been mainly grown on non-native substrates since 3C-SiC wafers have only been temporarily commercialized [61]. Silicon is one of the most-used substrates because of the low production cost and availability of large size. Nevertheless, the large mismatch in both lattice constants and thermal expansion coefficient becomes a challenge for obtaining high-quality 3C-SiC epitaxy. Defects, like anti-phase domains, stacking faults and voids, have very high density in grown 3C-SiC layers. In addition, epitaxy on (111) Si substrates turn out to have severe problems of warping and cracking. Thus, (001) oriented Si is preferred for using as substrates. A carbonization step during the growth is found to be very crucial for improving the quality of 3C-SiC epitaxy [62-66]. It is observed that a thin SiC layer is generated in this step and acts as a buffer for further growth [67]. This carbonization step was adapted to 3C-SiC grown on α -SiC substrates later,

which is also discussed in paper 1. Due to the limitations mentioned above for Si, α -SiC substrates attract researchers' attention. The DPBs defects emerge unfortunately. The elimination of this kind of defects becomes a hot research topic [68-73].

The aspect of GaN epitaxy

Substrate selection

Different types of substrates have strong influence on the final quality of GaN epitaxy, such as polarity, crystal orientation, strain, surface morphology and defect density [74]. Nowadays, GaN thin film for device applications is mainly heteroepitaxially grown on a non-native substrate. Nevertheless, with the development of bulk GaN, homoepitaxy growth gains more and more interest since the density of defects (e.g. threading dislocations (TD)) and stress could be largely reduced. In this section, we present several types of substrates for GaN epitaxy.

The first single crystalline *c*-plane GaN was directly grown on (0001) sapphire (Al_2O_3) substrate by HVPE [34]. But sapphire has around 15% mismatch of lattice constant with GaN, which generates a high density of dislocations [75]. The thermal expansion coefficient of sapphire is much larger than GaN, leading to compressive stress during the cooling procedure, which may result the deposited GaN to crack [76]. Furthermore, it has been reported that oxygen from the sapphire substrates could unintentionally dope the GaN epitaxial layer [77]. In order to improve the epitaxial layer quality, a nitridation step is often added before the growth in metalorganic CVD (MOCVD) and molecular beam epitaxy (MBE). It has been found that a thin layer of AlN is formed during this step [78, 79]. In fact, the growth of an AlN [80] or a low temperature GaN [81-83] buffer layer has been intentionally introduced at the initial stage to improve crystal

quality. Recently, research regarding GaN epitaxial layers grown on bulk AlN substrates have been reported [84].

Compared to sapphire, both 4H-SiC and 6H-SiC have a smaller mismatch of lattice constants and a better thermal conductivity [85]. The growth runs in paper 2, 3 and 4 are all made on 4H-SiC substrates. An AlN buffer is also needed between GaN layers and SiC substrates. Although SiC substrate has advantageous properties over a sapphire substrate, the grown GaN thin film still has high density of dislocation densities. One solution for this is to use bulk GaN substrate. The work in paper 5 and 6 is done on free-standing GaN substrates.

There are mainly four methods to produce bulk GaN single crystals. HVPE is the most popular way for free-standing GaN growth due to the very high growth rate (typical around 200 to 500 $\mu\text{m/h}$ in the c-direction) [86, 87] and low cost. The TD density could be decreased to around 10^4 - 10^6 cm^{-2} with increasing of GaN thickness [88]. In this vapor-phase growth technique, gallium chloride (GaCl) will be first synthesized by the reaction between metallic gallium and hydrogen chloride (HCl). Then GaN will be deposited on the seed crystal substrate after the ammonia gas is introduced to the reactor. High pressure solution growth (HPSG), ammonothermal and Na flux are all liquid solution growth methods [89]. The growth rates for these three methods are relatively low, around 1-10 $\mu\text{m/h}$ for HPSG [90], 2-3 $\mu\text{m/h}$ for ammonothermal growth [91] and approximately 30 $\mu\text{m/h}$ for Na-flux method [92], respectively. The obtained crystal quality is rather high although the production cost is still expensive at current stage.

The aspect of GaN epitaxy

Carbon doping of GaN

Semi-insulating (SI) buffer is a necessity for GaN-based transistors to isolate the active region of the device from the substrate. Carbon is often utilized to dope the GaN buffer to SI in CVD. The common way is to use the carbon atoms from the gallium precursor and control the carbon incorporation by modifying the CVD process parameters, i.e. temperature, pressure and gallium precursor flow rate. The incorporated carbon concentration will increase with decreased temperature, pressure and increased gallium precursor flow [93-95]. This kind of doping method is studied by quantum chemical and thermochemical modelling in paper 4. However, the CVD process might be operated in non-optimal conditions, which will give a bad thickness uniformity and rough morphology for the grown GaN epitaxial layers. In addition, carbon could also come from graphite insulation or from graphite susceptor part if the heat-resistant coating is damaged, which is very difficult to control. An alternative way for carbon doping is to tune the CVD process with very low residual carbon incorporation and intentionally adding a carbon precursor. The detailed information of precursor selection is discussed in paper 2. Propane is chosen to dope the GaN buffer layer in a HEMT structure, which is presented in paper 3.

4 Characterization

It's very important to examine the quality of epitaxial layers in order to improve the growth procedure. This chapter presents several most-used characterization techniques in this thesis.

4.1 Optical microscopy

Optical microscopy (Nikon Optihot 66) equipped with a Nomarski prism is used as a routine tool to check the morphology of samples quickly after growth (Fig. 4.1). It also could be utilized for measuring the thickness of hetero-epitaxial layers or even homo-epitaxial layers, if there is a difference in doping level compared to the substrates, by simply checking the cross section after cleaving the samples. The principle of the Nomarski prism is that it could split the incident light into two beams with orthogonal polarization. The two beams, which will have different optical paths after reflecting back from the sample, induce interference [96].

Figure 4.1 Optical microscopy images of (a) 3C-SiC hetero-epitaxial layer grown on an on-axis 4H-SiC substrate (b) 4H-SiC homo-epitaxial layer using a 1.28° off-cut substrate with the defect starting from a down fall.

4.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique applied to measure the samples' surface topography with a resolution of angstrom ($\text{\AA}$) scale. It was invented by Binnig, Quate, and Gerber from Stanford university and IBM in 1986 [97]. There're generally three operation modes of AFM, which are contact mode, non-contact mode and tapping mode. Tapping mode is chosen in this work to study the surface morphology of SiC and GaN. In this mode, the AFM probe, which comprises of a cantilever and a tip, will oscillate below or at the cantilever's resonance frequency. Figure 4.2 shows an example of AFM top view and cross section images of a 4H-SiC epitaxial layer. Its surface roughness is quantified by root mean square (RMS) value, i.e. surface height Z values' standard deviation in a certain area. The equation to calculate RMS value is listed as follows:

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}}$$

N : Number of points in a certain area

Z_i : Current Z value

Z_{ave} : Average Z value in a certain area

Figure 4.2 AFM top view (left) and cross section (right) images of a homo-epitaxial layer grown on a 4° 4H-SiC substrate (RMS = 2.611 nm). The growth was performed at 1565 $^\circ\text{C}$, 200 mbar using C_3H_8 and SiH_4 as precursors.

4.3 Photoluminescence

Photoluminescence (PL) measurement is a non-destructive technique. In my study, it was mainly applied to identify SiC polytypes [98], detect impurities and defects [99, 100], and quantify the concentration of dopants (for instance, Al and N in SiC) [101, 102]. The samples are attached on a holder of the cryostat and could be cooled down to around 2 K by liquid helium. A laser, which energy is larger than the band gap of measured material is used to excite the sample. Meanwhile, a monochromator is used to disperse and select the luminescence while a charge-coupled device (CCD) is applied to detect the luminescence. Figure 4.3 shows the typical low temperature PL near band gap emission spectrums for 3C-SiC and 4H-SiC.

Figure 4.3 PL spectrum at 2K of 3C-SiC and 4H-SiC near band gap emission.

Time-resolved photoluminescence (TRPL) technique is performed to study the optical properties of GaN in this thesis. In this measurement, the third harmonics ($\lambda = 266$ nm) of a Ti: sapphire femtosecond laser with a pulse frequency of 75 MHz is used for PL excitation. The emission signal is collected by optical lens into a monochromator and detected by a streak camera. The detected light's temporal profile is transformed to a spatial profile by streak camera and then collected by a CCD.

4.4 Cathodoluminescence

For cathodoluminescence (CL) characterization, a Galan MonoCL4 system is utilized. It is worth mentioning that CL technique is quite similar to PL. However, samples are excited by the electron beam from an SEM (LEO 1550 Gemini) in CL instead of a laser source in PL experiments. The generated CL signal could either be collected by a GaAs photomultiplier tube (PMT) detector or by a Si CCD detector. There are two operational modes, i.e. panchromatic mode and monochromatic mode, in CL spectroscopy. In the panchromatic mode, the detector records all the signals. However, in the monochromatic mode, only a particular emission wavelength is selected by a monochromator. The system could not only be used in room temperature, but also in low temperature after cooled by liquid helium. In CL imaging, the spatial resolution could be changed by using different SEM acceleration voltage [103].

Figure 4.4 shows the SEM and panchromatic CL images of a GaN epitaxial layer grown on a Ga-face GaN substrate. The measurement is done at room temperature using 5 kV acceleration voltage. The dark spots on the CL image are supposed to be associated with the pure screw type threading dislocations [104-107].

Figure 4.4 Room temperature SEM and panchromatic CL images of GaN homo-epitaxy using Ga-face GaN substrate.

4.5 X-ray diffraction

X-ray diffraction (XRD) is a non-destructive technique used for characterizing the crystal quality of epitaxial GaN and SiC layers in this thesis. There's no specific sample preparation procedure needed for this measurement. In 1913, William Henry Bragg and William Lawrence Bragg first published the well-known Bragg's Law, which is a description of the X-ray diffraction effect on crystal lattice [108]. The mathematical equation is written as follows:

$$n\lambda = 2d \sin \theta$$

where n is a positive integer representing the order of diffraction; λ is the wavelength of X-ray; d is the distance between two crystal planes; θ is the angle between an incident X-ray and the scattering plane [109].

An equipment “Empyrean” produced from a company called PANalytical was used to perform the XRD experiments. X-rays are emitted by bombarding a copper (Cu) anode. $K_{\alpha 1}$ X-ray ($\lambda = 1.54059 \text{ \AA}$) is finally used as the incident beam after other components, such as $K_{\alpha 2}$, K_{β} , are eliminated by the monochromator. Figure 4.5 illustrates the basic scan axis in XRD. The θ - 2θ scan, ω scan (rocking curve) and 2θ - ω scan are the mostly used scans in this work. This is because properties, such as lattice parameters and dislocation density, could be determined by analysing these scans [110].

Figure 4.5 A schematic figure of XRD diffractometer angles.

4.6 Secondary ion mass spectrometry

Secondary ion mass spectrometry (SIMS) is a useful technique to measure the impurity levels of the samples. All the SIMS measurements presented in the thesis were performed at Evans Analytical Group [111] using Cs^+ as primary ions to sputter the material. The detection limit for GaN material is around $1\text{--}2 \times 10^{16} \text{ cm}^{-3}$ for carbon, $5 \times 10^{15} \text{ cm}^{-3}$ for silicon and oxygen, respectively.

An example of the SIMS depth profile is shown in Fig. 4.6. The sample is an AlGaIn (20 nm) /GaIn ($1.7 \mu\text{m}$) structure deposited on a 4H-SiC substrate with an AlN buffer layer, which was grown at 1040°C , 50 mbar. The GaIn epitaxial layer has different carbon concentrations due to doped by different flow rate of propane (C_3H_8) gas.

Figure 4.6 SIMS depth profile of a sample with an AlGaIn/GaIn structure grown on a 4H-SiC substrate with an AlN buffer layer. The propane flow rate used in the figure is 0, 5, 10, 25, 50, 0 ml/min from left to right.

5 Summary of papers

In this PhD dissertation, several CVD solutions for the new directions in both SiC and GaN epitaxy have been provided, including 3C-SiC epitaxy on 4H-SiC substrates (paper 1), carbon doping of GaN (paper 2, 3 and 4), and epitaxy using free-standing GaN substrates (paper 5 and 6). A brief summary of the papers is listed as follows:

Paper 1

This paper, to the best of my knowledge, is the first work at the time when it's published showing standard CVD growth of high-quality 3C-SiC epitaxial layers on on-axis 4H-SiC substrates with large double-position-boundaries free area. Detailed investigation of the growth parameters' influence on the crystal quality of the 3C-SiC layers on on-axis 4H-SiC substrates has been clearly presented. Growth conditions, including temperature, C/Si ratio, ramp-up condition, Si/H₂ ratio, N₂ addition and pressure, are reproducible for the experiments.

Paper 2

Six different precursors utilized for intentional carbon doping of GaN in CVD, including methane (CH₄), acetylene (C₂H₂), ethylene (C₂H₄), propane (C₃H₈), iso-butane (i-C₄H₁₀) and trimethylamine (N(CH₃)₃), have been studied in detail by comparing the efficiency of carbon incorporation together with the influence on morphology and crystal quality. Computational fluid dynamic modeling of gas phase chemistry of the precursors has been used for a deeper understanding of the carbon incorporation species.

Paper 3

The epitaxial layers with a HEMT structure, which semi-insulating GaN buffer layer was doped by propane gas, were grown on a quarter of a 3-inch 4H-SiC

substrate. The epitaxial layers and final fabricated devices were characterized and assessed.

Paper 4

Computational fluid dynamic and ab initio quantum chemical calculations are compared with experimental results in order to explain the behaviour of carbon doping using carbon atoms from trimethylgallium ($\text{Ga}(\text{CH}_3)_3$).

Paper 5

The GaN layers have been homoepitaxially grown on N-face HVPE free-standing GaN substrates. The morphological, structural and optical properties of the grown layers are discussed. The smooth epitaxial layers could be grown by optimized parameters. It has shown that epitaxial layers have longer donor-bound exciton recombination time compared to the substrates.

Paper 6

Epitaxial layers with AlGaIn/GaN structures have been grown on both Ga-face and N-face free-standing HVPE GaN substrates. TRPL measurements are used to study the optical properties of the samples. The sample grown on the Ga-face substrate shows a PL line located at ~ 3.41 eV, which could be related to 2DEG emission.

6 My contribution to the papers

Paper 1

I have done most of the growth runs and characterization except XRD and PL.

I have written and finalized the paper with co-authors.

Paper 2

I have planned and done all the growth runs and all the related characterization, but not simulations. I have written and finalized the paper with co-authors.

Paper 3

I have done the growth and epitaxial layer characterization and taken part in the writing and the discussion of the manuscript.

Paper 4

I have done the growth experiments and taken part in the writing and the discussion.

Paper 5

I have planned and performed all the growth runs and characterization except PL measurements. I have written and finalized the paper with co-authors.

Paper 6

I have planned and performed all the growth runs and part of the characterization. I have written the manuscript with the help of the last author.

7 References

- [1] J. J. Berzelius, Ann. Phys. Lpz., **1**, 169 (1824).
- [2] A. G. Acheson, Engl. Patent 17911, (1892).
- [3] W. F. Knippenberg, Philips Research Reports, **18**, 161 (1963).
- [4] H. H. C. Dunwoody, U.S. Patent no. **837**, 616 (1906).
- [5] H. J. Round, Electrical world, **19**, 309 (1907).
- [6] J. A. Lely, Berichte der Deutschen Keramischen Gesellschaft, **32**, 229 (1955).
- [7] Yu. M. Tariov, V. F. Tsvetkov, J. Cryst. Growth, **43**, 209 (1978).
- [8] Yu. M. Tariov, V. F. Tsvetkov, J. Cryst. Growth, **52**, 146 (1981).
- [9] H. Matsunami, S. Nishino, H. Ono, IEEE Trans. Electron Devices, ED-28 (1981) 1235.
- [10] R. F. Davis, C. H. Carter Jr., C. E. Hunter, US patent No. Re 34,861 (1995).
- [11] A. Ellison, J. Zhang, J. Peterson, A. Henry, Q. Wahab, J. P. Bergman, Y. N. Makarov, A. Vorobev, A. Vehanen, E. Janzén, Materials Science and Engineering, B61-62, 113 (1999).
- [12] O. Kordina, C. Hallin, A. Ellison, S. Bakin, I. G. Ivanov, A. Henry, R. Yakimova, M. Tuominen, A. Vehanen, E. Janzén, Appl. Phys. Lett., **69**, 1456 (1996).
- [13] <http://www.cree.com/LED-Chips-and-Materials/Materials>
- [14] A. Schöner, M. Krieger, G. Pensl, M. Abe, and H. Nagasawa, Chem. Vap. Deposition, **12**, 523 (2006).
- [15] S. Yamasaki, T. Makino, D. Takeuchi, et al., Proc. of the ISPSD'13, Kanazawa, Japan, 2013, pp. 307-310.
- [16] H. Matsunami and T. Kimoto, Mat. Sci. Eng. R, **20**, 125 (1997).
- [17] A. A. Lebedev and V. E. Chelnokov, Semiconductors, **33**, 999 (1999).
- [18] P. G. Neudeck, Inst. Phys. Conf. Ser., **141**, 1 (1994).

- [19] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, *J. Appl. Phys.*, **76**, 1363 (1994).
- [20] F. Roccaforte, F. Giannazzo, F. Iucolano, J. Eriksson, M. H. Weng, and V. Raineri, *Appl. Surf. Sci.*, **256**, 5727 (2010).
- [21] V. E. Chelnokov and A. L. Syrkin, *Mater. Sci. Eng. B*, **46**, 248 (1997).
- [22] R. F. Davis, *Inst. Phys. Conf. Ser.*, **137**, 1 (1994).
- [23] L. S. Ramsdell, *Am. Mineral.*, **32**, 64 (1947).
- [24] F. La Via, *Silicon Carbide Epitaxy*, chapter 9, IBSN: 978-81-308-0500-9 (2012).
- [25] M. Leroux, B. Gil, in: J. H. Edgar, S. S. Strite, I. Akasaki, H. Amano (Eds.), *INSPEC, The Institution of Electrical Engineers*, Stevenage, UK (1999) p. 45.
- [26] D. C. Look, J. R. Sizelove, *Appl. Phys. Lett.*, **79**, 1133 (2001).
- [27] D. I. Florescu, V. M. Asnin, F. H. Pollak, A. M. Jones, J. C. Ramer, M. J. Schurman, I. Ferguson, *Appl. Phys. Lett.*, **77**, 1464 (2000).
- [28] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, T. Yamada, and T. Mukai, *Jpn. J. Appl. Phys.*, **34**, L1332 (1995).
- [29] Z. M. Zhao, R. L. Jiang, P. Chen, D. J. Xi, Z. Y. Luo, R. Zhang, B. Shen, Z. Z. Chen, and Y. D. Zheng, *Appl. Phys. Lett.*, **77**, 444 (2000).
- [30] D. Walker, E. Monroy, P. Kung, J. Wu, M. Hamilton, F. J. Sanchez, J. Diaz, and M. Razeghi, *Appl. Phys. Lett.*, **74**, 762 (1999).
- [31] J. C. Carrano, T. Li, D. L. Brown, P. A. Grudowshi, C. J. Eiting, R. D. Dupuis, and J. C. Campbell, *Appl. Phys. Lett.*, **73**, 2405 (1998).
- [32] S. J. Pearton and F. Ren, *Adv. Mater.*, **12**, 1571 (2000).
- [33] W. C. Johnson, J. B. Parsons, and M. C. Crew, *J. Phys. Chem.*, **36**, 2651 (1932).
- [34] H. P. Maruska and J. J. Tietjen, *Appl. Phys. Lett.*, **15**, 327 (1969).
- [35] J. I. Pankove, E. A. Miller, D. Richman, and J. E. Berkeyheiser, *J. Lumin.*, **4**, 63 (1971).

- [36] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, *Jpn. J. Appl. Phys.*, **28**, L2112 (1989).
- [37] http://www.nobelprize.org/nobel_prizes/physics/laureates/2014/press.html
- [38] J. M. Edgar (Ed.), *Properties of Group III Nitrides*, IBSPEC, Institution of Electrical Engineers, London (1994).
- [39] H. Selke, V. Kirchner, H. Heinke, S. Einfeldt, P.L. Ryder, and D. Hommel, *J. Cryst. Growth*, **208**, 57 (2000).
- [40] H. J. Lee, H. Ryu, and C. Lee, K. Kim, *J. Cryst. Growth*, **191**, 621 (1998).
- [41] B. Gil, *Group III Nitride Semiconductor Compounds*, Clarendon Press, Oxford (1998) p. 417.
- [42] F. Bernardini, V. Fiorentini, and D. Vanderbilt, *Phys. Rev. B*, **56**, R10024 (1997).
- [43] H. Jeong, S. Y. Jeong, D. J. Park, H. J. Jeong, S. Jeong, J. T. Han, H. J. Jeong, S. Yang, H.Y. Kim, K. Baeg, S. J. Par, Y. H. Ahn, E. Suh, G. Lee, Y. H. Lee, and M. S. Jeong, *Sci. Rep.*, **5**, 7778 (2015).
- [44] O. Ambacher, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, W. J. Schaff, L. F. Eastman, R. Dimitrov, L. Wittmer, M. Stutzmann, W. Rieger, and J. Hilsenbeck, *J. Appl. Phys.*, **85**, 3222 (1999).
- [45] O. Ambacher, B. Foutz, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, A. J. Sierakowshi, W. J. Schaff, L. F. Eastman, R. Dimitrov, A. Mitchell, and M. Stutzmann, *J. Appl. Phys.*, **87**, 334 (2000).
- [46] S. Keller, H. Li, M. Laurent, Y. Hu, N. Pfaff, J. Lu, D. F. Brown, N. A. Fichtenbaum, J. S. Speck, S. P. DenBaars, and U. K. Mishra, *Semicond. Sci. Technol.*, **29**, 113001 (2014).
- [47] R. D. Dupuis, *J. Cryst. Growth*, **178**, 56 (1997).
- [48] A. C. Jones, and M. L. Hitchman, *Chemical Vapour Deposition, Precursors, Processes and Applications*, Royal Society of Chemistry (2009), ISBN: 978-0-85404-465-8.
- [49] E. Bauer, *Z. Krist.*, **110**, 372 (1958).

- [50] A. A. Burk, Chem. Vap. Deposition, **12**, 465 (2006).
- [51] F. La Via, Silicon Carbon Epitaxy, Chapter 1, (2012) ISBN: 978-81-308-0500-9.
- [52] O. Kordina, C. Hallin, A. Henry, J. P. Bergman, I. Ivanov, A. Ellison, N. T. Son, and E. Janzén, phys. stat. sol. (b), **202**,321 (1997).
- [53] O. Kordina, A. Henry, E. Janzén, and C. H. Carter Jr., Mat. Sci. Forum, **264-268**, 97 (1998).
- [54] Ö. Daneilsson, C. Hallin, and E. Janzén, J. Cryst. Growth, **252**, 289 (2003).
- [55] Ö. Danielsson, U. Forsberg, A. Henry, and E. Janzén, J. Cryst. Growth, **235**, 352 (2002).
- [56] A. Henry, J. Hassan, J. P. Bergman, C. Hallin, and E. Janzén, Chem. Vap. Deposition, **12**, 475 (2006).
- [57] H. N. Jaytirtha, and M. G. Spencer, Materials Research Society Symposium Proceedings, **410**, 329 (1996).
- [58] M. Portail, A. Michon, S. Vézian, D. Lefebvre, S. Chenot, E. Roudon, M. Zielinski, T. Chassagne, A. Tiberj, J. Camassel, and Y. Cordier, J. Cryst. Growth, **349**, 27 (2012).
- [59] J. Pezoldt, R. Grieseler, T. Schupp, D. J. As, and P. Schaaf, Mater. Sci. Forum, **717-720**, 513 (2012).
- [60] Y. Abe, N. Ohmori, A. Watanabe, J. Komiyama, S. Suzuki, H. Fujimori, H. Nakanishi, and T. Egawa, J. Cryst. Growth, **318**, 460 (2011).
- [61] H. Nagasawa, K. Yagi, and T. Kawahara, J. Cryst. Growth, **237-239**, 1244 (2002).
- [62] H. Khan, and R. N. Summergrad, Appl. Phys. Lett., **11**, 12 (1967).
- [63] J. P. Li, and A. J. Steckl, J. Electrochem. Soc., **142**, 634 (1995).
- [64] R. Scholz, U. Gösele, F. Wischmeyer, and E. Niemann, Appl. Phys. A, **66**, 59 (1998).
- [65] Kusunoki, Jpn. J. Appl. Phys. Lett., **32**, 2074 (1993).
- [66] Addiamano, and H. Klein, J. Cryst. Growth, **10**, 291 (1984).

- [67] G. Ferro, Crit. Rev. Solid State Mater. Sci., **40**, 56 (2015).
- [68] H. S. Kong, J. T. Glass, and R. F. Davis, J. Mater. Res., **4**, 204 (1989).
- [69] M. Soueidan, G. Ferro, O. Kim-Hak, F. Cauwet, and B. Nsouli, Cryst. Growth Des., **8**, 1044 (2008).
- [70] K. Nishino, T. Kimoto, and H. Matsunami, Jpn. J. Appl. Phys., **36**, 5202 (1997).
- [71] F. R. Chen, S. R. Nutt, W. S. Yoo, T. Kimoto, and H. Matsunami, J. Cryst. Growth, **137**, 175 (1994).
- [72] J. Lorenzzi, M. Lazar, D. Tournier, N. Jegenyes, D. Carole, F. Cauwet, and G. Ferro, Cryst. Growth Des., **11**, 2177 (2011).
- [73] P. G. Neudeck, A. J. Trunek, D. J. Spry, J. A. Powell, H. Du, M. Skowronski, X. R. Huang, and M. Dudley. Chem. Vap. Deposition, **12**, 531 (2006).
- [74] L. Liu, and J. H. Edgar, Mat. Sci. Eng. R, **37**, 61 (2002).
- [75] F. A. Ponce, in: B. Gil (Ed.), Group III Nitride Semiconductor Compounds, Oxford University Press, Oxford (1998) p.123.
- [76] E. V. Etzkorn, and D. R. Clarke, J. Appl. Phys., **89**, 1025 (2001).
- [77] J. E. Van Nostrand, J. Solomon, A. Saxler, Q. H. Xie, and D. C. Look, J. Appl. Phys., **87**, 8766 (2000).
- [78] M. Yeadon, M. T. Michael, F. Hamdani, S. Pekin, H. Morkoç, and J. M. Gibson, J. Appl. Phys., **83**, 2847 (1998).
- [79] T. Hashimoto, Y. Terakoshi, M. Yuri, M. Ishida, O. Imafuji, T. Sugino, and K. Itoh, J. Appl. Phys., **86**, 3670 (1999).
- [80] H. Amano, N. Sawaki, I. Akasaki, and Y. Toyoda, Appl. Phys. Lett., **48**, 353 (1986).
- [81] V. Kirchner, R. Ebel, H. Heinke, S. Einfeldt, D. Hommel, H. Selke, P. L. Ryder, Mater. Sci. Eng. B, **59**, 47 (1999).
- [82] T. Wang, T. Shirahama, H. B. Sun, H. X. Wang, J. Bai, S. Sakai, and H. Misawa, Appl. Phys. Lett., **76**, 2220 (2000).

- [83] L. Sugiura, K. Itaya, J. Nishio, H. Fujimoto, and Y. Okubun, *J. Appl. Phys.*, **82**, 4877 (1997).
- [84] S. B. Schujman, L. J. Schowalter, R. T. Bondokov, K. E. Morgan, W. Liu, J. A. Smart, and T. Bettles, *J. Cryst. Growth*, **310**, 887 (2008).
- [85] A. D. Hanser, R. F. Davis, in: J. H. Edgar, S. S. Strite, I. Akasaki, H. Amano (Eds.), *Properties, Processing and Applications of Gallium Nitride and Related Semiconductors*, INSPEC, The Institution of Electrical Engineers, Stevenage, UK, (1999) p.386.
- [86] C. Hemmingsson, and G. Pozina, *J. Cryst. Growth*, **366**, 61 (2013).
- [87] B. Łucznik, B. Pastuszka, I. Grzegory, M. Bockowski, G. Kamler, E. Litwin-Staszewska, and S. Porowski, *J. Cryst. Growth*, **281**, 38 (2005).
- [88] R. P. Vaudo, X. Xu, C. Loria, A. D. Salant, J. S. Flynn, and G. R. Brandes, *Phys. Status Solidi A*, **194**, 494 (2002).
- [89] D. Ehrentraut, and Z. Sitar, *MRS BULL.*, **34**, 259 (2009).
- [90] J. Karpinski, S. Porowski, and S. Miotkowska, *J. Cryst. Growth*, **56**, 77 (1982).
- [91] B. Wang, and M. J. Callahan, *Cryst. Growth Des.*, **6**, 1227 (2006).
- [92] H. Amano, *Jpn. J. Appl. Phys.*, **52**, 050001 (2013).
- [93] G. Parish, S. Keller, S. P. Denbaars, and U. K. Mishra, *J. Electron. Mater.*, **29**, 15 (2000).
- [94] A. Ishibashi, H. Takeishi, M. Mannoh, Y. Yabuuchi, and Y. Ban, *J. Electron. Mater.* **25**, 799 (1996).
- [95] D. D. Koleske, A. E. Wickenden, R. L. Henry, and M. E. Twigg, *J. Cryst. Growth*, **242**, 55 (2002).
- [96] D. K. Schroder, *Semiconductor material and device characterization*, John Wiley & Sons, Inc. (2006).
- [97] Veeco SPM Training Notebook.
- [98] R. P. Devaty and W. J. Choyke, *Phys. Stat. Sol. (a)*, **162**, 5 (1997).
- [99] L. Patrick and W. J. Choyke, *Phys. Rev. B*, **10**, 5091 (1974).

- [100] A. Henry, C. Hallin, I. G. Ivanov, J. P. Bergman, O. Kordina, U. Lindefelt, and E. Janzén, *Phys. Rev. B*, **53**, 13503 (1996).
- [101] I. G. Ivanov, C. Hallin, A. Henry, O. Kordina, and E. Janzén, *J. Appl. Phys.*, **80**, 3504 (1996).
- [102] J. Camassel, S. Juillaguet, M. Zielinski, and C. Balloud, *Chem. Vap. Deposition*, **12**, 549 (2006).
- [103] MonoCL4 (including Plus, Swift and Elite) User Guide.
- [104] C. Hemmingsson, G. Pozina, *J. Cryst. Growth*, **366**, 61 (2013).
- [105] E. G. Braze, M. A. Chin, V. Narayanamurti, *Appl. Phys. Lett.*, **74**, 2367 (1999).
- [106] G. Koley, M. G. Spencer, *Appl. Phys. Lett.*, **78**, 2873 (2001).
- [107] T. Hino, S. Tomiya, T. Miyajima, K. Yanashima, S. Hashimoto, M. Ikeda, *Appl. Phys. Lett.*, **76**, 3421 (2000).
- [108] W. H. Bragg and W. L. Bragg, *Proc. R. Soc. Lond. A*, **88**, 428 (1913).
- [109] M. Birkholz, *Thin Film Analysis by X-Ray Scattering*, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (2006).
- [110] M. A. Moram and M. E. Vickers, *Rep. Prog. Phys.*, **72**, 036502 (2009).
- [111] <http://www.eag.com>

Part II: Papers

Papers

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-117878>