

Characterisation of scandium- and iron-
based GaN for high electron mobility
transistors (HEMTs)

By

Simona Pace

Department of Materials

Imperial College London

A Thesis submitted in fulfilment of the requirements for the degree of Doctor of
Philosophy of Imperial College London

October 2018

*To all my teachers,
in school and life.*

Declaration of Originality

The work presented in this thesis is my own and any information reported in text and figures obtained from other authors have been properly referenced. This thesis has been checked for plagiarism using Turnitin on the 30.09.2018 and 12.10.2018.

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purpose. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Abstract

III-nitrides have received increasing attention for high electron mobility transistors (HEMTs), due to their structural and electrical properties. The AlGa_N/Ga_N structure shows large band offset and can generate 2D physically-confined channel at its interface. However, the performance of these devices is still limited by defects and impurities present in the structure. The former act as electron-traps in the channel, while the latter generate unwanted background carriers.

To overcome this problem, scandium- and iron-based Ga_N materials have been proposed. When Sc is introduced in Ga_N, the c/a ratio decreases, and the band gap increases, leading to a new set of lattice-parameter/band-gap ratios. Such that, ScGa_N/Ga_N may show large band offset with lower concentration of defects. Furthermore, the large piezoelectric constant of ScGa_N should increase the carrier concentration in the channel. The background conductivity can be improved by introducing a (Fe,Ga)_N layer at the Ga_N/sapphire interface. Fe introduces acceptor-like states in the band gap, leading to semi-insulating behaviour and improved channel-confinement.

In this work the properties of Ga_N, ScGa_N and (Fe,Ga)_N grown using e-beam physical vapour deposition are investigated. The optimal Ga e-beam currents were found and epitaxial growth of Ga_N with relatively good quality achieved. ScGa_N with increasing Sc concentration was also investigated. Large structural improvement was found for Sc 20%, possibly due to some relation between ScGa_N and sapphire lattice parameters that reduces the stress in the thin film. In agreement with theoretical results, the band gap of Sc_{0.2}Ga_{0.8}N increases by 0.2 eV.

Finally, the homogeneity and resistivity of (Fe,Ga)_N were investigated. When Fe is 0.8% the structural quality is not affected while the resistivity increases to $10^8 \Omega \text{cm}^{-2}$. For higher Fe concentration, Fe-rich nanocrystals become visible. However, no relation between inhomogeneity and electrical properties is observed and when Fe is 4.6% the resistivity further increases by 1 order of magnitude.

Acknowledgments

It is my pleasure to take this occasion to thank all the people who helped me during these years and this adventure.

First and mostly, I would like to thank my supervisors Prof. Neil Alford and Dr Michelle Moram, for this incredible opportunity and for showing me how a scientist can be resilient, passionate and creative.

I would also like to thank Prof. David Ritchie and the Semiconductor Physics group at University of Cambridge for hosting me during the second half of my PhD and for helping me during my visit. My gratitude goes also to the Cambridge Centre for GaN in University of Cambridge, for kindly agreeing to let me use their laboratories for TEM samples preparations. Moreover, I would like to thank Jesus College for hosting me during my first months in Cambridge.

In addition, I would like to thank Leverhulme Trust for funding this project and my education during these three years.

I would also like to thank Dr Peter Petrov, Dr Robert Davies and Dr Bin Zou for growing the samples used in this work and for their prompt advice any time I needed.

I would also like to express my gratitude to all the people who advised me during my experimental work both at Imperial College London and University of Cambridge; in particular I would like to thank Dr Richard Langford, Dr Sneha Rhode, Dr Giorgio Divitini, Dr Sarah Fearn, Dr Menno Kappers, Mr Richard Sweeney, Dr Victoria Bemmer and Miss Becky Kilmurray.

Also, I would like to take this occasion to thank Imperial College London and University of Cambridge as institutions, for making me feel always welcome and safe in these times of uncertainties.

Finally, I would like to thank my family, their love for me is and will always be my greatest strength.

Publications and Conferences

Publications

- *“ScGaN grown using e-beam PVD: structural and optical characterisation”*

In final composition

- *“Structural and electrical properties of Fe-doped GaN grown using e-beam PVD”*

In composition

Conferences

- *“Structural and electronic characterisation of III-IV nitride materials ScGaN”*,
S. Pace, R.J. Davies, M.A. Moram. ICNS12 conference (2017), Strasbourg (France) – Poster presentation.
- *“Structural and optical characterisation of ScGaN”*,
S. Pace, R.J. Davies, M.A. Moram. EUROMAT17 conference (2017), Thessaloniki (Greece) – Oral presentation.
- *“Structural and optical characterisation of ScGaN grown using e-beam PVD”*,
S. Pace, R.J. Davies, M.A. Moram. UKNC conference (2018), Manchester (UK) – Oral presentation.
- *“Characterisation of ScGaN, FeGaN and FeScGaN as alternative materials for high electron mobility transistors (HEMTs)”*,
S. Pace, B. Zou, R.J. Davies, M.A. Moram. MRS18 spring meeting (2018), Phoenix (USA) – Oral presentation.
- *“Semi-insulating FeGaN grown using e-Beam PVD: structural and electrical characterisation”*
S. Pace, B. Zou, M.A. Moram, JEUMAT18 (2018), Budapest (Hungary) – Oral presentation.

Table of Contents

Abstract.....	4
Acknowledgments.....	5
Publications and Conferences	6
List of Figures	10
List of Tables	16
Chapter 1	18
Introduction.....	18
1.1 Overview and motivation.....	18
1.2 Nitride materials.....	23
1.2.1. GaN and other III-nitrides.....	23
1.2.2. Transition metal nitrides (TMNs)	27
1.2.2.1. ScGaN and ScAlN	29
1.2.2.2. (Fe,Ga)N	35
1.3 Growth techniques	40
1.3.1. Metalorganic chemical vapour deposition (MOCVD).....	40
1.3.2. Molecular beam epitaxy (MBE).....	43
1.3.3. Electron-beam physical vapour deposition (e-beam PVD).....	45
1.4 High electron mobility transistor (HEMT)	48
1.4.1. HEMT working principle and 2D electron gas (2DEG)	48
1.4.2. Device operation and figure of merit	50
1.4.3. HEMT limitations	52
Chapter 2.....	54
Experimental techniques.....	54
2.1 Introduction.....	54
2.2 Epitaxial Growth.....	54
2.3 Structural and morphological characterisation.....	55
2.3.1 Atomic force microscopy (AFM).....	55
2.3.2 X-ray Diffraction (XRD)	57
2.3.3 Transmission electron microscopy (TEM).....	61
2.4 Secondary ion beam mass spectroscopy (SIMS)	70
2.5 Optical characterisation.....	73
2.5.1 Ultraviolet-visible Transmittance and Reflectance spectrophotometry	73
2.5.2 Photoluminescence spectroscopy.....	75

2.6	Raman spectroscopy	77
2.7	Electrical characterisation	81
2.7.1	Hall effect measurements	81
Chapter 3		86
Characterisation of GaN		86
3.1	Introduction	86
3.2	Growth rate	87
3.3	Surface morphology	89
3.4	Structural and microstructural characterisation	92
3.5	Optical characterisation and band gap	100
3.5.1	Transmittance spectroscopy	100
3.5.2	Photoluminescence spectroscopy	103
3.6	Conclusions	104
Chapter 4		106
Characterisation of ScGaN		106
4.1	Introduction	106
4.2	Growth rate	107
4.3	Determination of Sc concentration	109
4.4	Surface morphology	114
4.5	Structural and microstructural characterisation	116
4.6	Raman spectroscopy	123
4.7	Optical characterisation and band gap	124
4.7.1.	Transmittance spectroscopy	124
4.7.2.	Reflectance spectroscopy	126
4.8	Photoluminescence spectroscopy	127
4.9	Conclusions	128
Chapter 5		130
Characterisation of (Fe,Ga)N		130
5.1	Introduction	130
5.2	Determination of Fe concentration and structure homogeneity	131
5.3	Surface morphology	133
5.4	Structural and microstructural characterisation	135
5.5	Raman spectroscopy	143
5.6	Optical characterisation	145
5.6.1.	Transmittance spectroscopy	145
5.6.2.	Photoluminescence spectroscopy	148
5.7	Electrical characterisation	150

5.8	Conclusions.....	152
Chapter 6.....		155
	Conclusions and future work	155
6.1	Conclusions.....	155
6.2	Future work.....	159
References.....		162
Appendix A.....		176
	Growth conditions.....	176
Appendix B		177
	TEM sample preparation.....	177
Appendix C		179
	Permission to reproduce third party work.....	179

List of Figures

Figure 1. 1 Electrical properties of Silicon and other wide-bandgap materials. (Data from Table 1.1).	19
Figure 1. 2 Schematic representation of GaN-based HEMT basic structure. The 2DEG channel is obtained at the interface between GaN and AlGaIn.	21
Figure 1. 3 Schematic representation of wurtzite structure of GaN. Modified from Qin et al. [25] DOI: https://doi.org/10.3390/ma10121419 .	24
Figure 1. 4 Relationship between bandgap, lattice parameter a and composition in the continuous alloy system AlN/GaN/InN. Image reproduced and adapted from Zhang et al. [32], DOI: https://doi.org/10.1063/1.4824179 .	25
Figure 1. 5 Schematic representation of stacking fault I_1 , I_2 , and E present in wurtzite structures along the $\langle 1120 \rangle$ direction. Upper and lower case refers to cations and anions, respectively. Reproduced and adapted from Potin et al. [51], DOI: https://doi.org/10.1088/0953-8984/12/49/332 , with © IOP Publishing permission. All rights reserved.	27
Figure 1.6 Schematic representation of the most common crystal structure of transition metal nitrides (TMNs): rock-salt face-centred cubic (a), hexagonal closed packed (b) and simple hexagonal (hex) structures. Reused and adapted from Zhong et al. [52], DOI: https://doi.org/10.1002/advs.201500286 .	28
Figure 1. 7 Schematic representation of hexagonal wurtzite-like structure of ScN calculated. Reprinted Figure with permission from N. Farrer, L. Bellaiche Phys. Rev. B, 66 pp. 201203-201206 (2002) Copyright 2002 by the American Physical Society [62], DOI: https://doi.org/10.1103/PhysRevB.66.201203 .	30
Figure 1. 8 Mixing enthalpy diagrams of ScGaIn (green) and ScAlIn (blue) for Sc concentration moving from 0 to 100 %. Reproduced from S. Zhang et al. [32] with AIP Publishing permission, DOI: https://doi.org/10.1063/1.4824179 .	31
Figure 1. 9 HR TEM images of GaN (a) and ScGaIn with Sc concentration of 5 % (b) and 37 % (c). The increment of Sc concentration leads to generation of defects lowering the quality of the interface. Reprinted from Constantin et al. [64] with AIP Publishing permission, DOI: https://doi.org/10.1063/1.2140889 .	32
Figure 1. 10 Expanded plot of variation of band gap and lattice parameter a with composition in ternary III-nitride materials. When Sc is introduced in AlIn system the band gap decreases, while the lattice parameter a increases. When Sc is introduced in GaIn both the lattice parameter a and the band gap increase. The calculated lattice parameter and band gap of wurtzite ScN (wz-ScN) is also shown. Reproduced from Zhang et al. [32] with AIP Publishing permission, DOI: https://doi.org/10.1063/1.4824179 .	32
Figure 1. 11 Band structure calculated for binary AlIn, ScAlIn and ScN (a) and GaIn, ScGaIn and ScN (b) with Sc concentration of 12.5 % and 25 %. The red arrows highlight the minimum conduction bands and the maximum valence bands of the materials. Reproduced from Zhang et al. [32] with AIP Publishing permission, DOI: https://doi.org/10.1063/1.4824179 .	33
Figure 1. 12 a) Qualitative representation of Fe^{3+} states in the tetrahedral crystal field of wurtzite structure (reproduced and adapted from Malguth et al. [78], with John Wiley and Sons permission, DOI:	

<https://doi.org/10.1002/pssb.200743315>; b) schematic representation of the mechanism of [$^4T_1(G) - ^6A_1(S)$] luminescence transition (reproduced and adapted from Figure 2 in Dumcenco et al. [82], DOI: <https://doi.org/10.1063/1.3592343>).....37

Figure 1. 13 a) HR-TEM image of (Ga,Fe)N nanocrystals embedded in GaN matrix (Reproduced Figure from Bonanni et al Phys. Rev. B, vol. 75, p. 125210 (2007) [79]. Copyright 2007 by the American Physical Society, DOI: <https://doi.org/10.1103/PhysRevB.75.125210>). b) EDS spectra of (Ga,Fe)N thin films taken around the nanocrystal (Spectrum 3) and in the GaN matrix (Spectrum 4) (Reproduced Figure from Bonanni et al Phys. Rev. B, vol. 75, p. 125210 (2007) [79]. Copyright 2007 by the American Physical Society, DOI: <https://doi.org/10.1103/PhysRevB.75.125210>).....39

Figure 1. 14 a) Simplified representation of Growth mechanism of GaN thin film in a MOCVD system. In this representation the precursors (TMGa and NH_3) are introduced as gas flow using inert gas carriers (1). Once in the growth chamber they may first react in gas phase (2). The intermediate species then adsorb on the surface of the substrate (3) and react leading to the nucleation of GaN (4). Finally, volatile by-products are removed using exhaust tubes (5). b) schematic representation of a Thomas Swan CCS MOCVD reactor (reproduced from E.J. Thrush [100]).....42

Figure 1. 15 Schematic representation of a molecular beam epitaxy (MBE) system. Reprinted from P. Ruterana et al., “Nitride Semiconductors: Handbook on Materials and Devices”, chapter 3, (2006), with the permission of John Wiley and Sons Publishing [101], DOI: <https://doi.org/10.1002/3527607641>. 44

Figure 1. 16 Different growth regimes of GaN grown in PA-MBE obtained by using different III/V ratios and growth temperatures. Reprinted from H. Morkoç, “Handbook of Nitride Semiconductors and Devices: Materials Properties, Physics and Growth, Volume 1”, Chapter 3, (2009), with the permission of John Wiley and Sons Publishing [107], DOI: <https://doi.org/10.1002/9783527628438>. 45

Figure 1. 17 Photographs of the e-beam PVD system in Imperial College London used for the thin film growth in this work.....46

Figure 1. 18 Schematic representation of the main chamber (a) and the working principle (b) of the electron-beam physical vapour deposition (e-beam PVD). The electron beam is generated by heating a tungsten filament (1), then it is focused (2) to impact on the centre of the crucible (3). This impact causes the evaporation of particles of the target material that eventually reach the heated substrate (5) where they react.....47

Figure 1. 19 a) simplified representation of a GaN-based HEMT device. b) representation of the bending of band structure at the AlGaIn/GaN interface. The 2DEG lies below the Fermi level in these structures. Reprinted from A survey of gallium nitride HEMT for RF and high power applications, Superlattice. Microst., 109 (2017), pp. 519-537, A.S. Fletcher et al. Copyright (2017), with permission from Elsevier [9], DOI: <https://doi.org/10.1016/j.spmi.2017.05.042>. 49

Figure 1. 20 Schematic representation of spontaneous and piezoelectric polarisations present in AlGaIn and GaN in HEMT structures. Modified from S. Helkman et al. [23] with AIP permission, DOI: <https://doi.org/10.1063/1.1577222>. 50

Figure 1. 21 Measured current (I) vs Applied voltage (V) of a generic HEMT transistor for different applied gate voltages.....51

Figure 2. 1 Schematic representation of an AFM system used in tapping mode [123].....56

Figure 2. 2 Scheme of the conditions necessary to satisfy Bragg's law for a set of planes. Reprinted from Moram et al. [127], DOI: https://doi.org/10.1088/0034-4885/72/3/036502 , © IOP Publishing. With permission. All rights reserved.	58
Figure 2. 3 Schematic illustration of an HR-XRD diffractometer used for thin film characterisation.	59
Figure 2. 4 X-ray spectrum showing the energy of electrons accelerated onto the copper anode. The sharp peaks are K_{α} and K_{β} , which are obtained by the falling of an electron from the L to the K shell of the copper atom. The underlying broad peak is the Bremsstrahlung radiation, due to the deceleration of electrons.	59
Figure 2. 5 Representation of the scattering events that can happen in the TEM when the electron beam interacts with the specimen. Reprinted by permission from Springer: Springer Nature, "Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 3 Scattering and diffraction" by D.B. Williams, C.B. Carter, (2009) Copyright. With permission of Springer Publishing. DOI: https://link.springer.com/book/10.1007/978-0-387-76501-3 [129]	61
Figure 2. 6 Schematic representation of the component of a TEM used in imaging (a) and diffraction (b) modes.	63
Figure 2. 7 Section of the reciprocal space in which part of the Ewald sphere and two rows of lattice relrods are shown. Only the relrods that intercept the Ewald sphere give rise to diffraction spots with different intensities.	64
Figure 2. 8 Cross-sectional TEM bright-field (a) and dark-field (b) images close to the [1120] zone axis of GaN thin film. Reused from Wong et al. [130] with AIP permission, DOI: https://doi.org/10.1063/1.3009669	65
Figure 2. 9 Cross-section high resolution TEM images of GaN close to the [1120] zone axis of GaN thin film.	66
Figure 2. 10 Schematic representation of a TEM used in STEM mode: using a focused C2 lens the electron beam is converged and only a small area of the sample is illuminated. Reprinted by permission from Springer: Springer Nature, "Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 9 The instrument" by D.B. Williams, C.B. Carter, (2009) Copyright https://link.springer.com/book/10.1007/978-0-387-76501-3 [129].	68
Figure 2. 11 Mechanism of generation of characteristic X-ray photons used to obtain EDX spectra.	70
Figure 2. 12 Schematic representation of a ToF-SIMS system. Reused from Fearn et al. [131] with author permission, DOI: https://doi.org/10.1088/978-1-6817-4088-1	71
Figure 2. 13 Band gap extrapolation using the Tauc plot (a) and the Kubelka-Munk function (b). The former is obtained from Transmittance data and the thickness of the sample, while the latter is calculated using Reflectance data. In both cases, the band gap is obtained from the linear extrapolation of the curve and is equal to the energy value for y equal to 0.	74
Figure 2. 14 Schematic representation of possible photoluminescence processes.	76
Figure 2. 15 Photoluminescence spectra of GaN at room temperature. The sharp peak is related to the band gap transition, while the broader band gap at larger wavelength is caused by the presence of defects or impurities in the structure.	77
Figure 2. 16 Energy spectrum of electromagnetic wave expressed as wavenumber, wavelength and frequency.. The different spectroscopies used to analyse different portion of the wave are reported in the table. Reprinted from Introductory Raman Spectroscopy – Chapter 1, Elsevier book., J. R. Ferraro, Kazuo Nakamoto, Chris W. Brown Copyright (2003), with permission from Elsevier [139], DOI: https://doi.org/10.1016/B978-0-12-254105-6.X5000-8	78

Figure 2. 17 Possible phonon modes present in a GaN wurtzite structure. Reprinted from Hiroshi Harima 2002 J. Phys.: Condens. Matter, 14, R967, © IOP Publishing. All rights reserved [141], DOI: https://doi.org/10.1088/0953-8984/14/38/201	80
Figure 2. 18 Schematic representation of the Raman spectrometer structure.	81
Figure 2. 19 Schematic representation of the Hall effect in a p-type semiconductor. Reprinted by permission from Springer: Springer Nature, “Electrical characterization of semiconductor materials and devices—review” – Deen, M.J. & Pascal, F. J Mater Sci: Mater Electron (2006) 17: 549, (2006) Copyright. [143], DOI: https://doi.org/10.1007/s10854-006-0001-8	82
Figure 2. 20 Schematic representation of Hall bar geometries for Hall measurement [144].	83
Figure 2. 21 Different Van der Pauw geometries for Hall measurement [144].....	84
Figure 3. 1 Growth rate plot of GaN grown using different Ga e-beam currents. The dependence of the growth rate on the e-beam current used suggests that the growth takes place in N-rich conditions.....	88
Figure 3. 2 1x1 μm AFM images of GaN grown using Ga e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e). All AFM the images are processed using parabolic flattening.	90
Figure 3. 3 Nanocrystallite size (a) and root-mean-square roughness (b) of GaN grown using increasing Ga e-beam current measured from AFM images illustrate in Figure 3.2.....	91
Figure 3. 4 Bright-field (BF) (a) and centred-dark-field (CDF) (b) plan-view TEM images of GaN grown using Ga e-beam current equal to 82 mA.	91
Figure 3. 5 2θ - ω scans of GaN grown using e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e).	93
Figure 3. 6 ω scans of GaN grown using e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e).....	94
Figure 3. 7 Bright field TEM images obtained along the [1100] and [1120] zone axes, respectively, of GaN grown using e-beam current equal to 73 (a-b), 76 (c-d), 79 (e-f), 82 (g-h) and 85 mA (i-l). Black arrows were used to highlight the triangular pits present on the surfaces of GaN grown using intermediate e-beam currents (c-h).....	96
Figure 3. 8 High resolution TEM images taken along the [1120] zone axis of GaN grown using e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e). The red (1) and yellow (2) insets highlight the regions of the structure near the GaN/sapphire interfaces and the near-surface areas respectively.....	98
Figure 3. 9 c/a ratios obtained for TEM diffraction patterns of GaN grown using increasing Ga e-beam currents. .	99
Figure 3. 10 Transmittance spectra of GaN grown using e-beam current equal to 73 (A), 76 (B), 79 (C), 82 (D) and 85 mA (E).	101
Figure 3. 11 Calculated Tauc plots (a) of GaN grown using e-beam current equal to 76 (B), 79 (C), 82 (D) and extrapolated band gaps (b).	102
Figure 3. 12 Photoluminescence spectra (a) of GaN grown using e-beam current equal to 76 (B), 79 (C), 82 (D) and extrapolated band gaps (b).	103
Figure 4. 1 Plot of growth rate vs of Sc/Ga e-Beam current ratio. The substrates were all heated at 850 °C and the p_{N_2} is maintained at 1×10^{-4} tor.....	108

Figure 4. 2 SIMS depth profile with positive (a) and negative (b) polarity of GaN thin film grown using MOCVD.	110
Figure 4. 3 SIMS depth profile with positive polarity of GaN grown using MOCVD (a) and e-beam PVD (b) and ScGa _N grown using e-beam PVD (c). The spike levels of Ga ⁺ and Sc ⁺ registered at the first few seconds of the analysis are an artefact of the technique and visible in both e-beam PVD thin films, as well as the MOCVD GaN reference.	111
Figure 4. 4 Simplified representation of the relation between amount of exposed surface and SIMS depth profile of surface impurities, such as oxygen or silicon.	112
Figure 4. 5 Depth profiles of ScGa _N thin films of Sample D (a) and E (b) expressed as a function of Ga and Sc percentages vs sputtering depth.	113
Figure 4. 6 STEM-HAADF images taken at the 1120 zone axis of Sc _x Ga _{1-x} N with x equal to 0.012 (a), 0.20 (b), showing no evident composition segregation.	114
Figure 4. 7 2x2 μm ² and 1x1 μm ² AFM height images of GaN (a-b) and Sc _x Ga _{1-x} N with x equal to 0.02 (c-d), 0.12 (e-f) and 0.20 (g-h). All the images are processed using parabolic flattening.	115
Figure 4. 8 Root-mean-square (RMS) (a) and nanocrystal size (b) values for GaN and ScGa _N thin films extrapolated from AFM data.	116
Figure 4. 9 2θ–ω scan of GaN (sample A) (a) and ScGa _N thin films with different Sc concentrations (samples C-E) (b-d).	117
Figure 4. 10 ω scan of GaN (sample A) (a) and ScGa _N with 12 % (b) and 20 % (c) of Sc.	119
Figure 4. 11 Bright field TEM images of GaN (a) and Sc _x Ga _{1-x} N with x equal to 0.05 (b), 0.12 (c) and 0.20 (d). The images are taken at the 1120 zone axis using a 20-cm objective aperture.	120
Figure 4. 12 High-resolution TEM images of GaN (a) and Sc _x Ga _{1-x} N with x equal to 0.05 (b), 0.12 (c) and 0.20 (d). The images are taken at the 1120 zone axis using a 50-cm objective aperture.	121
Figure 4. 13 Aberration-corrected HR-STEM images of the interface between sapphire and ScGa _N thin film in Sample E.	122
Figure 4. 14 Raman spectra of GaN and ScGa _N thin films (a) and zoom-in on GaN-related E ₂ peak at 568 cm ⁻¹ (b). Sapphire peaks are highlighted by the star.	123
Figure 4. 15 E ₂ ^H positions of GaN and ScGa _N calculated from the Raman spectra shown in Figure 4.14.	124
Figure 4. 16 Transmittance spectra of GaN and ScGa _N with Sc concentration of 12 and 20 %.	125
Figure 4. 17 Tauc plot (a) and extrapolated band gap values (b) of samples A, D and E.	125
Figure 4. 18 Reflectance spectra of GaN and ScGa _N with 12 and 20 % of Sc.	126
Figure 4. 19 Kubelka-Munk plot (a) and extrapolated band gap values (b) of samples A, D and E.	127
Figure 4. 20 Room temperature photoluminescence spectra for GaN (a) and ScGa _N thin films with Sc of 5 % (b), 12 % (c) and 20 % (d).	128

Figure 5. 1 STEM images and EDX maps of Fe-doped GaN grown using Fe e-beam current 20 (a-c) and 56 mA (d-g). The relative mass spectra and Ga and Fe concentration are reported for both Fe-doped GaN grown using lower (d) and higher (h) Fe e-beam current.	132
Figure 5. 2 High-resolution STEM images (a-b) and EDX maps (c-d) of a nanocrystal observed in Sample C. The relative EDX spectrum is shown in e.	133
Figure 5. 3 5x5 μm^2 and 2x2 μm^2 AFM height images of UID GaN (a-b) and Fe-doped GaN with Fe concentration equal to 0.008 (c-d) and 0.046 (e-f). All the images are processed using parabolic flattening.	134
Figure 5. 4 HR-XRD $2\theta-\omega$ scans of UID GaN (a) and Fe-doped GaN with 0.8 % (b) and 4.6 % (c). The peaks related to the secondary phases present in Fe-doped GaN with higher concentration of Fe (c) are highlighted with black arrows.	136
Figure 5. 5 Slower HR-XRD $2\theta-\omega$ with increased signal-to-noise ratio between 40 and 60 ° of Fe-doped GaN with Fe concentration equal to 0.8 % (a) and 4.6 % (b).	137
Figure 5. 6 rocking curves obtained from HR-XRD ω scans of UID GaN (a) and Fe-doped GaN with 0.8 % (b) and 4.6 % (c). The full-width-half-maximum (FWHM) values of these curves are also reported.	138
Figure 5. 7 Bright field TEM images of UID GaN (a) and Fe-doped GaN with Fe concentration equal to 0.8 % (b) and 4.6 % (c). The images are taken at the 1100 zone axis using a 20-cm objective aperture.	139
Figure 5. 8 High-resolution TEM images taken at the near-surface, within-the-film and near-interface areas of UID GaN (a-c) and Fe-doped GaN with Fe concentration equal to 0.8 % (d-f) and 4.6 % (g-i). The images are taken at the 1120 zone axis using a 40-cm objective aperture.	140
Figure 5. 9 High-resolution TEM images nanocrystals observed in Fe-doped GaN with Fe concentration equal 4.6 %. According to d spacing in this Fe-doped GaN α -Fe (a-b) and ζ -Fe ₂ N (c-d) are present in the GaN matrix. The images are taken at the 1100 zone axis using a 40-cm objective aperture.	142
Figure 5. 10 Raman spectra of UID GaN (a) and Fe-doped GaN with Fe concentration 0.8 % (b) and 4.6 % (c).	143
Figure 5. 11 E_2^H peak trend as a function of Fe concentration in UID and Fe-doped GaN thin films extrapolated from Raman spectra.	145
Figure 5. 12 Transmittance spectra of UID GaN and Fe-doped GaN thin films in the range between 200 and 800 nm.	146
Figure 5. 13 Tauc plot of UID GaN and Fe-doped GaN (a) calculated from the transmittance spectra illustrated in Figure 5.12 and the extrapolated band gap values (b).	148
Figure 5. 14 Photoluminescence spectra of UID GaN (a) and Fe-doped GaN with Fe concentration equal to 4.6 % (b).	149
Figure 5. 15 Sheet resistivity (a) and sheet carrier resistivity (b) plots of UID and Fe-doped GaN obtained from Hall measurements.	152

List of Tables

Table 1. 1 Electrical properties of Si and other wide-bandgap materials [3]. Copyright (2006) The Japan Society of Applied Physics, DOI: https://doi.org/10.1143/JJAP.45.7565	19
Table 1. 2 Figures of merit (FoM) relevant of high-power, high-frequency and high-voltage applications of GaN and GaAs materials [3]. (E_c : Electric breakdown voltage, v_{sat} : saturation velocity, κ : thermal conductivity, ϵ : dielectric constant, μ : electron mobility). The values are calculated using silicon performance as reference. Copyright (2006) The Japan Society of Applied Physics, DOI: https://doi.org/10.1143/JJAP.45.7565	21
Table 1. 3 Lattice parameters c/a ratio and internal parameter values for ideal wurtzite structure and III-nitride materials GaN, AlN and InN at 300 K. Reproduced from Rinke et al. “Consistent set of band parameters for the group-III nitrides AlN, GaN, and In”, DOI: https://doi.org/10.1103/PhysRevB.77.075202 , [26].	24
Table 1. 4 Properties of GaN and other substrates commonly used to grow GaN thin films. *TEC: thermal expansion coefficient [43]. Reproduced with IEEE permission, © (2012) IEEE, DOI: https://doi.org/10.1109/SMElec.2012.6417246	26
Table 3. 1 Ga e-beam currents, thicknesses and growth rate of all GaN samples under study. The thickness was calculated using cross-section TEM imaging.	88
Table 3. 2 Position of (002) peaks measured from 2θ – ω scans of GaN grown using increasing Ga e-beam current. The calculated c parameters and strain in the thin films are also reported.	92
Table 3. 3 Full-width-half-maximum values of GaN obtained from the fitting of (002) peak in 2θ – ω and ω scans	94
Table 4. 1 In the table the Sc/Ga e-Beam ratio, the estimated scandium content and the growth rate for all samples are reported.	108
Table 4. 2 Concentrations of Sc in ScGa _N samples as estimated from the Sc/Ga e-beam ratio and from the SIMS depth profiles.	113
Table 4. 3 (002) peak positions and calculated c lattice parameters and calculated strain level are reported for ScGa _N with increasing concentration of scandium.	118
Table 4. 4 Band gap values of Samples A, D and E obtained using Absorption spectra, Tauc Plot and Kubelka-Munk function.	127
Table 5. 1 (002) peak position measured using 2θ – ω scans, calculated c lattice parameter and out of plane strain of UID and Fe-doped GaN thin films.	138
Table 5. 2 c/a ratios of UID and Fe-doped GaN thin films calculated from the TEM diffraction patterns.	142
Table 5. 3 Positions of Raman peaks of UID GaN and Fe-doped GaN with Fe concentration equal to 0.8 % and 4.6 % extrapolated from Raman spectra illustrated in Figure 5.10.	144
Table 5. 4 Optical properties of UID and Fe-doped GaN calculated from the interference fringes.	147

Table A. 1 e-beam PVD growth conditions used to grow GaN using increasing Ga e-beam current (Chapter 3)	176
Table A. 2 e-beam PVD growth conditions used to grow ScGa ₂ N using increasing Sc e-beam current (Chapter 4)	176
Table A. 3 e-beam PVD growth conditions used to grow ScGa ₂ N using increasing Fe e-beam current (Chapter 5)	176

Chapter 1

Introduction

1.1 Overview and motivation

Over the last 60 years, electronic devices, such as computers and smartphones, have become fundamental in every aspect of our daily life. However, because of the constant demand for smaller, faster and higher-performance devices, the silicon-based industry is now approaching its theoretical limits. Since the invention of the first transistor in 1954 [1], silicon has been used as main material in the electronics production, mainly due to its low cost and relatively simple fabrication procedures. However, despite these great economic advantages, silicon is not the ideal candidate for electronic and optical applications: although cheap, silicon is an indirect semiconductor with a band gap as narrow as 1.1 eV, with low saturation velocity and low breakdown voltage [2]. These intrinsic properties limit the theoretically-achievable performance of the final transistor in terms of operating power, frequencies and temperatures.

With the aim of addressing this problem, increasing attention has been recently devoted to the research of alternative materials that might be able to overcome these limits. Wide-bandgap materials, such as SiC, GaAs and GaN, are promising candidates to replace silicon in the electronics industry. As shown in Figure 1.1 and summarized in Table 1.1, these wide-bandgap materials show superior properties to

silicon, in terms of wider bandgaps, which allow higher operating temperatures, higher breakdown voltages, which permit working at higher voltages, and higher electron saturation velocities, which are necessary for high-frequency and high-power devices. However, although these superior electrical properties should theoretically lead to improved transistor performance, several experimental challenges must be overcome before silicon can be fully replaced by these wide-bandgap materials.

	Si	SiC	GaAs	GaN
Bandgap (eV)	1.12	3.26	1.43	3.39
Electric breakdown voltage (kV/cm)	300	2000	400	3300
Electron saturation velocity ($\times 10^7$ cm ² /V s)	1.0	2.0	2.0	2.25
Thermal conductivity ($\times 10^2$ W/m K)	1.5	4.5	0.5	1.3
Dielectric permeability (ϵ_r)	11.8	10	12.8	9

Table 1. 1 Electrical properties of Si and other wide-bandgap materials [3]. Copyright (2006) The Japan Society of Applied Physics, DOI: <https://doi.org/10.1143/JJAP.45.7565>.

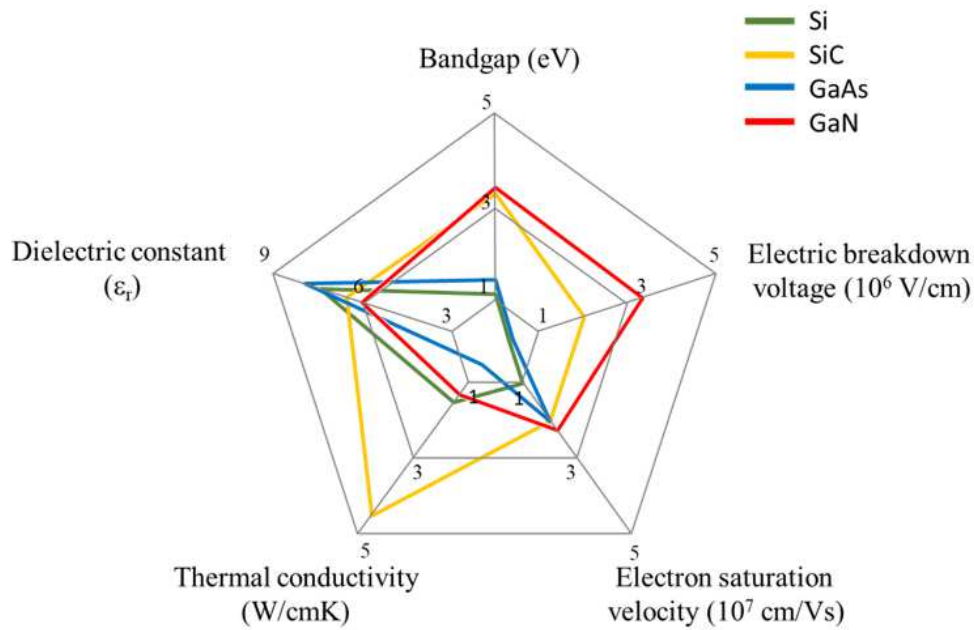


Figure 1. 1 Electrical properties of Silicon and other wide-bandgap materials. (Data from Table 1.1).

Among these alternative materials, SiC provides the most mature technology and, because of its remarkably high thermal conductivity, is widely used in high-power applications. However, currently at least, its high fabrication costs and small size substrates make it unsuitable for large-scale industry production. Since the invention of the first high electron mobility transistor (HEMT) in 1979 [4], GaAs has been widely used in high-frequency applications. In addition to good electronic properties, the main advantage of using GaAs in transistor fabrication is its ability to grow in complex heteroepitaxial structures that lead to the spatial confinement of the electron channel in a 2D electron gas (2DEG). This spatial confinement greatly increases the concentration and mobility of the electrons in the channel, resulting in remarkable performance of the transistor in high-frequency applications. However,

although GaAs-based transistor fabrication is now well established, the relatively narrow bandgap (1.43 eV) and the low breakdown voltage (400 kV/cm) put a limit to the performance that GaAs-based HEMT can achieve, particularly in high-power and high-voltage applications. For this reason, GaN has recently received increasing attention as a promising substitute for GaAs in HEMT technology. GaN, as well as GaAs, is a III-V semiconductor and is able to grow in complex epitaxial structures necessary to obtain the 2DEG channel. Furthermore, GaN has a much wider bandgap (3.4 eV) and higher breakdown voltage (3 300 kV/cm) than GaAs, properties that make it a more suitable candidate for high-power, high-frequency and high-voltage HEMTs.

To quantify the advantage of using GaN in high-power, high-frequency and high-voltage applications, several figures of merit can be used, and the most relevant ones are reported in Table 1.2. Johnson's figure of merit (FoM) [5] is calculated as the product between the breakdown voltage (E_c) and the saturation velocity (v_{sat}) and it can give an estimation of the power that a transistor can handle when used at high frequencies and low voltages. Key's FoM [6] is important for high-temperature applications, and it is based on the thermal conductivity (κ), saturation velocity (v_{sat}) and dielectric constant (ϵ) of the material. This FoM is used to estimate the thermal limit of a device in high-temperature applications. Finally, Baliga's FoM [7] and HFoM [8] are the indicators of transistor power loss at low and high frequencies, respectively. The Baliga's FoM is given by the product between dielectric constant (ϵ), electron mobility (μ) and breakdown voltage (E_c) and it is used to evaluate the power loss at low frequencies, when the main cause is the current dissipation in the on-resistance region. The HFoM, instead, is a more general form of Baliga's FoM, in which the switching losses are also taken into account. Therefore, HFoM is a more suitable FoM to evaluate power losses if the device is used at higher frequencies. Comparing the figures of merit calculated for GaN and GaAs in Table 1.2, in which silicon performance are used as reference, it is evident that GaN is a more suitable candidate for high-power, high-frequency applications. The superior electrical properties of GaN have resulted in promising HEMT performance, and GaN-based HEMT devices with record cut-off frequency of 2.02 THz, while maintaining breakdown voltage higher than 18 V, have been reported in literature [9]. Because of these promising results, GaN-based HEMTs are now studied for a wide range of applications, such as RF amplifier [10], wireless communication systems [11], radars and space microwave transmissions [12], among others. However, GaN technology has not reached its full potential yet and a number of issues still need to be fixed.

	Formula	Si	GaAs	GaN
Johnson's FoM	$\frac{E_c v_{sat}}{2\pi}$	1	7.1	760
Keyes FoM	$\kappa \left(\frac{v_{sat}}{\varepsilon} \right)^{1/2}$	1	0.45	1.6
Baliga's FoM	$\varepsilon \mu E_c^3$	1	15.6	650
Baliga's HFoM	μE_c^2	1	10.8	77.8

Table 1. 2 Figures of merit (FoM) relevant of high-power, high-frequency and high-voltage applications of GaN and GaAs materials [3]. (E_c : Electric breakdown voltage, v_{sat} : saturation velocity, κ : thermal conductivity, ε : dielectric constant, μ : electron mobility). The values are calculated using silicon performance as reference. Copyright (2006) The Japan Society of Applied Physics, DOI: <https://doi.org/10.1143/JJAP.45.7565>.

One of the major issues of GaN-based HEMTs is the presence of electron-traps and scattering-centres in the 2DEG channel that reduce the mobility and concentration of electrons. As shown in Figure 1.2, the main structure of a GaN-based HEMT consists of a thick layer of GaN and a thinner layer of a wider bandgap material, such AlGaN. Because of the wider bandgap of AlGaN, a heterojunction is generated at the interface where the electrons are confined in a 2DEG [13]. However, when Al is introduced in the GaN system, the lattice parameters change along with the Al concentration. When AlGaN is grown on the top of GaN, then, this variation in lattice parameters results in a certain degree of stress and strain in the AlGaN layer, which usually relaxes through generation of defects or cracking at the interface. These defects at the interface are believed to act as electron traps that lower the concentration and mobility of electron in the 2DEG [14]. Therefore, it is of great importance to improve the quality of the AlGaN/GaN interface in order to further improve the performance of GaN-based HEMT devices.

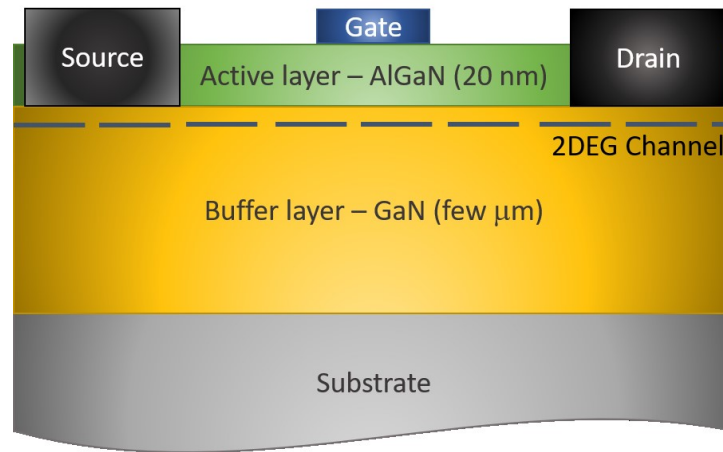


Figure 1. 2 Schematic representation of GaN-based HEMT basic structure. The 2DEG channel is obtained at the interface between GaN and AlGaN.

Great effort has been made to reduce the concentration of defects at the interface between GaN and AlGaN, and different approaches have been proposed [15]–[18]. For instance, it has been found that the performance of AlGaN/GaN HEMT devices can be improved by adding very thin interlayers of AlN between GaN and AlGaN [15], [19]. The introduction of these thin layers, in fact, gives the double

advantage to increase the smoothness of the interface, reducing the electron scattering at the interface, and to increase the band offset at the AlN/GaN interface, deepening the quantum well where the 2DEG is generated. Another interesting approach includes the use of nanopatterned substrates to reduce the concentration of defects in GaN thin film [16], [20]. If GaN is grown on the top of a nanopatterned substrates, the concentration of defect in the thin film is drastically reduced, leading to improved quality of the AlGaIn/GaN interface. However, despite the numerous adjustments that have been proposed to improve the quality of the AlGaIn/GaN interface, at the moment none of them appear to fully solve this problem, leaving GaN-based HEMT performances still far from their theoretical limits.

This lack of breakthrough discovery has encouraged the research into alternative materials that might be able to replace AlGaIn in the HEMT structure and improve the performance of GaN-based devices. To successfully replace AlGaIn in the HEMT structure, it is necessary that the candidate material has suitable electrical and structural properties: it must have large band gap, so that the band offset at the interface is large enough to obtain high concentrations of electrons in the 2DEG channel; suitable electronic properties, so that the electrons in the 2DEG are well confined and current leakage is avoided; suitable lattice parameters, so that the generation of defects at the interface is suppressed.

An interesting candidate that might be able to meet these requirements and replace AlGaIn in HEMT structures is ScGaIn. ScGaIn is a transition metal nitride (TMN) obtained by mixing cubic ScN and wurtzite GaN. Because of the instability between the wurtzite and the cubic phases, ScGaIn shows unique properties, such as high piezoelectric constant, large band gap, and good lattice-match with GaN [21]. Hence, these properties make ScGaIn a valid candidate for alternative HEMT structures.

Another problem that affects GaN-based HEMTs, is the presence of parasitic background carrier concentrations arising from donor impurities present in the nitride structure. This background conductivity reduces the performance of HEMT devices, especially in high-power and high-frequency applications. Therefore, it is important to improve the insulation level of the device and suppress any leakage current present in the layers of the HEMT device. One method to achieve this insulation is by using semi-insulating materials, such as (Fe,Ga)N, that are able to compensate these background carriers present in GaN. To obtain this insulation, (Fe,Ga)N and related materials are usually grown at the GaN/sapphire interface so that the *n*-type conductivity in GaN is suppressed. However, the insulation of the channel might also be improved via co-doping of the active layer, possibly obtained using quaternary FeAlGaIn or FeScGaIn.

To successfully employ these alternative materials in HEMT devices, however, it is first necessary to achieve deep knowledge of both their electrical and structural properties. Therefore, in this work a comprehensive characterisation of the transition metal nitrides ScGaIn and FeGaIn is carried out, with the aim to find possible alternative materials for enhanced HEMT devices.

1.2 Nitride materials

1.2.1. GaN and other III-nitrides

III-nitrides are a class of materials of great interest for both optical and electronic applications. The interest for these materials is mostly due to their direct, wide bandgap and their short bond lengths in the structure, resulting in highly stable materials even under extreme conditions [3]. In optical and electronic applications, the most popular materials of this class are certainly GaN, AlN, InN and their alloys AlGaN and InGaN. In this section, crystal structure, defects and optical and electrical properties of GaN and related III-nitrides are reported.

GaN, AlN and InN can crystallize in wurtzite, zinc-blend or rock-salt cubic structures, however in standard conditions the wurtzite structure is the most stable with space group $P6_3mc$. As shown in Figure 1.3, the wurtzite structure is obtained by stacking Ga (or Al or In) and N atoms along the $[000\bar{1}]$ direction following an ...ABABA... sequence [22]. In each layer, Ga (or N) atoms are surrounded by 4 N (or Ga) atoms in a tetrahedral geometry, giving either a Ga- or a N-polar surface [23]. The final polarity of the crystal can be selected by carefully choosing growth conditions, substrates and nucleation layers. Since different polarities lead to different mechanical and electronic properties, the final polarity of the crystal structure is particularly important for optical and electronic applications: Ga-polar thin films are usually preferred over N-polar thin films, mostly due to their higher resistance to etchant materials.

Generally, a wurtzite structure can be fully described by using four parameters: a and c lattice parameters, their ratio c/a and the internal parameter u , which can be defined as the ratio between the bond length b and the lattice parameter along the c axis [24]. The values for GaN, AlN and InN wurtzite structures are reported in Table 1.3. As shown in this Table, the c/a ratios of these III-nitrides differ from the ratio of the ideal wurtzite structure. This deviation from the ideal value is mainly due to the size of ions in the structure and the length of the bond with nitrogen. Since the space group of these III-nitride materials ($P6_3mc$) is non-centrosymmetric, this deviation from the ideal c/a ratio generates a certain degree of internal spontaneous polarization (P_{SP}) in the structure [24]. As discussed later in this chapter, this spontaneous polarization has a major role in the generation of the 2D electron gas and, therefore, is of particular interest for optical and electronic devices.

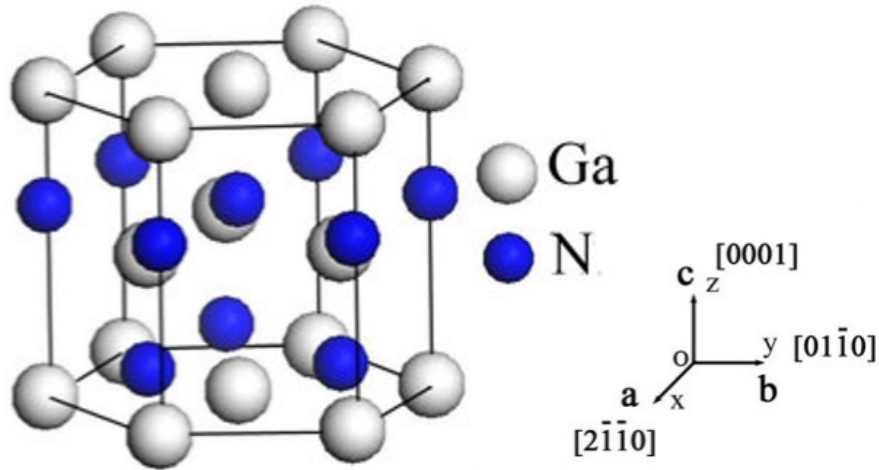


Figure 1. 3 Schematic representation of wurtzite structure of GaN. Modified from Qin et al. [25] DOI: <https://doi.org/10.3390/ma10121419>.

	Ideal wurtzite structure	AlN	GaN	InN
Lattice parameter a_0 (Å)	-	3.110	3.190	3.540
Lattice parameter c_0 (Å)	-	4.980	5.189	5.706
c_0/a_0 ratio	1.633	1.6013	1.6266	1.6120
Internal parameter u	-	0.382	0.377	0.380

Table 1. 3 Lattice parameters c/a ratio and internal parameter values for ideal wurtzite structure and III-nitride materials GaN, AlN and InN at 300 K. Reproduced from Rinke et al. "Consistent set of band parameters for the group-III nitrides AlN, GaN, and In", DOI: <https://doi.org/10.1103/PhysRevB.77.075202>, [26].

As mentioned earlier in this chapter, one of the properties that makes these III-nitride materials very interesting for optical and electronic applications is their wide bandgap. However, another unique feature of these materials is their ability to generate a continuous alloy system, in which the resultant ternary (or quaternary) alloys are stable in wurtzite structure and show a direct bandgap for any composition [27]. As shown in Figure 1.4, the lattice parameters and the value of the bandgap depend on the composition of the alloy. Therefore by carefully choosing the composition of this alloy the bandgap can be tuned from 0.7 eV (InN) to 6.2 eV (AlN) [28]. The ability to engineer the bandgap of these materials, so that the emission wavelength can change from 1800 nm (InN) to 200 nm (AlN), makes them the perfect candidates for optical devices emitting in the entire visible range, such as light emitting diodes (LED) and laser diodes (LDs) [29]–[31]. In addition, the direct nature of their bandgap enhances the rate of electron-hole recombination, improving the performance of these optical devices.

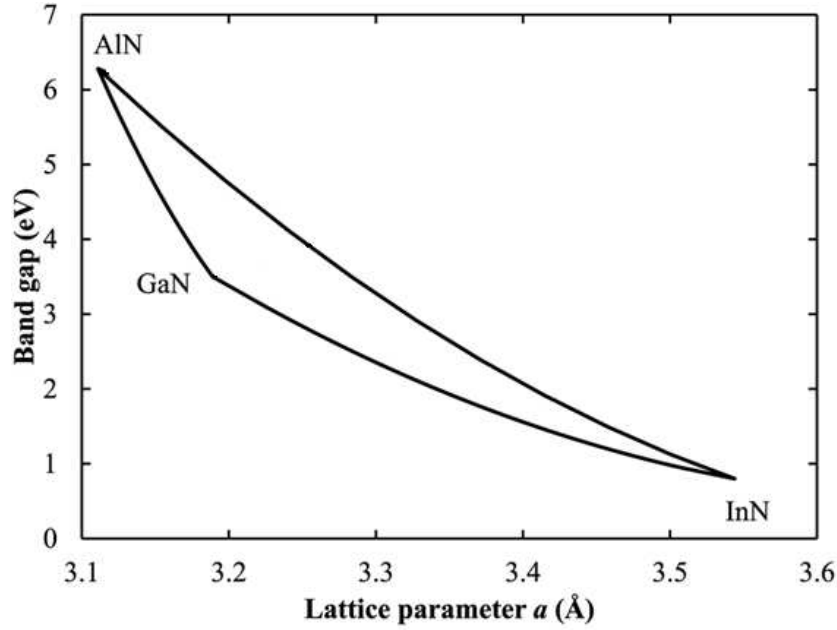


Figure 1. 4 Relationship between bandgap, lattice parameter a and composition in the continuous alloy system AlN/GaN/InN. Image reproduced and adapted from Zhang et al. [32], DOI: <https://doi.org/10.1063/1.4824179>.

In addition, unintentionally doped GaN usually shows n -type conductivity with electron concentrations of the order of 10^{18} cm^{-3} . This n -type behaviour is probably a result of oxygen or other impurities unintentionally incorporated during the growth [33]–[35] or of the presence of N vacancies in the structure. To further increase the concentration of electrons up to 10^{19} cm^{-3} , GaN is usually doped with silicon, which can be easily incorporated in the GaN structure without affecting the crystal quality [36]. Recently, increasing attention has also been devoted to the growth of p -type GaN. This p -type behaviour is usually obtained by doping GaN with elements stable in +2 oxidation state, such as Mg, Zn, C or Be; however, because of the intrinsic n -type behaviour of GaN, achieving p -type conductivity without effecting the carrier mobility had been very challenging for long time [37]–[40], limiting the performance of early GaN-based LED devices. In 1992 Nakamura and co-worker [41], [42] have suggested that the low p -type doping yield in GaN was caused by the presence of dopant-hydrogen complexes in GaN structure. During the growth in MOCVD, in fact, hydrogen is often used as carrier and can react with dopants, such as Mg, to generate complexes electrically inactive. In addition, Nakamura and collaborators have also shown that these hydrogen-based complexes can be dissociated by simply annealing or irradiating the sample, generating Mg-doped GaN with large p -type conductivity. Based on this method, p -type GaN is now routinely grown and largely used in LED, lasers and electronic devices.

Although the properties of these III-nitride materials are promising and several GaN-based optical and electronic devices are already commercially available, numerous problems are still present. One of the major problems is the lack of a high-quality, inexpensive GaN substrate. The use of an intrinsic substrate, such as GaN, would be the ideal choice for high-quality, defect-free thin films. However, because of the high costs of production and the small wafer-sizes available, GaN thin films are usually

grown on the top of external substrates, such as silicon, SiC or sapphire. In Table 1.4, the structural properties and costs of GaN and other substrates are reported. SiC is clearly the most expensive choice, however it also has the smallest lattice mismatch with GaN (4 %) and the smallest thermal expansion coefficient (TEC) mismatch (3.25 %) [43]. Because of these small mismatches, the concentration of defects in GaN thin films grown on SiC is much lower ($10^8 - 10^{10} \text{ cm}^{-2}$) than in GaN grown on other substrates. However, this concentration is still high enough to affect the performance of the final electronic devices. On the other hand, silicon is the cheapest substrate and is available in wafers as large as 12 inches. However, the lattice and the TEC mismatches are as large as 17 % and 56 %, respectively. These large mismatches result in poor quality of the GaN thin films and great improvement is still necessary before GaN grown on Si can be competitive in optical and electronic applications [44]. Finally, sapphire (Al_2O_3) is another substrate commonly used to grow GaN. Compared to SiC and silicon substrates, sapphire has intermediate lattice (16 %) and TEC (39 %) mismatches and can be bought in wafer as large as 8 inches at moderate cost. The lattice mismatch leads to high concentration of defects up to 10^{10} cm^{-2} , which lowers the performance of the final device in terms of carrier mobility and minor carrier lifetime. However, because of the moderate cost and the relatively good quality of GaN thin films, sapphire is usually chosen as substrate for laboratory experiments and development research [45].

Material	Lattice mismatch to GaN (%)	Thermal conductivity at 300K (W/mK)	TEC mismatch to GaN (%)	Wafer sizes and cost
GaN	0	130	0	Up to 2'' Very expensive
SiC	4	490	3.2	Up to 6'' Very expensive
Silicon	17	150	56	Up to 12'' Not expensive
Sapphire	16	30	39	Up to 8'' Moderately expensive

Table 1. 4 Properties of GaN and other substrates commonly used to grow GaN thin films. *TEC: thermal expansion coefficient [43]. Reproduced with IEEE permission, © (2012) IEEE, DOI: <https://doi.org/10.1109/SMElec.2012.6417246>.

As mentioned above, these defects present in GaN grown on external substrates can be of different types and generally arising from the lattice and TEC mismatches between GaN and the chosen substrate. The most common defects observed in GaN and other III-nitrides materials are linear defects, such as misfit and threading dislocations, and planar defects, such as stacking faults. Misfit dislocations are usually generated when the lattice mismatch between two films is larger than a maximum value and the strain is relaxed via generation of defects [46]. For instance, these dislocations are often visible at the interface between GaN and InGaN or AlGaIn, due to the variation of lattice parameters with the alloy composition (Figure 1.4). However, when a very thin layer of InGaIn (or AlGaIn) is grown on the top of GaN, a pseudomorphic InGaIn film is first observed, in which the lattice parameters match the GaN ones and the structure remains under stress. This pseudomorphic film remains stable up to a certain thickness, known as the critical thickness, which depends on the degree of lattice mismatch, the growth

conditions and the structure of the compounds. If the pseudomorphic film is thicker than the critical thickness, then it must relax by generation of misfit dislocations or cracking [46], [47]. Another type of dislocation usually observed in III-nitrides is the threading dislocation. In a GaN thin film grown on sapphire, the concentration of these threading dislocations is generally in the range of $10^8 - 10^{10} \text{ cm}^{-2}$ [48]. These threading dislocations usually appear at the very beginning of the growth and propagate throughout the film; however, the origin and generation mechanism of these dislocation is yet not clear. This type of dislocations is believed to be one of the major causes of device fault, although their role is still not completely understood [14], [49].

Planar defects, such as stacking faults, are also very common in III-nitride thin films. These defects are generated when the wurtzite stacking sequence ...ABABAB... is no longer respected and a layer of atoms is introduced or removed. Depending on how the stacking sequence is interrupted, the stacking fault can be of three different types: intrinsic I_1 , in which one basal plane is removed and the sequence becomes ...ABABCBCB..., intrinsic I_2 , in which two basal planes are removed, or two cubic rows are introduced, and the stacking sequence is ...ABABCACA..., or extrinsic E , in which a complete sequence of cubic structure is introduced in the wurtzite sequence, in this case the sequence becomes ...ABABCABA... [50], [51]. In Figure 1.5 the representations of the three types of stacking fault are shown.

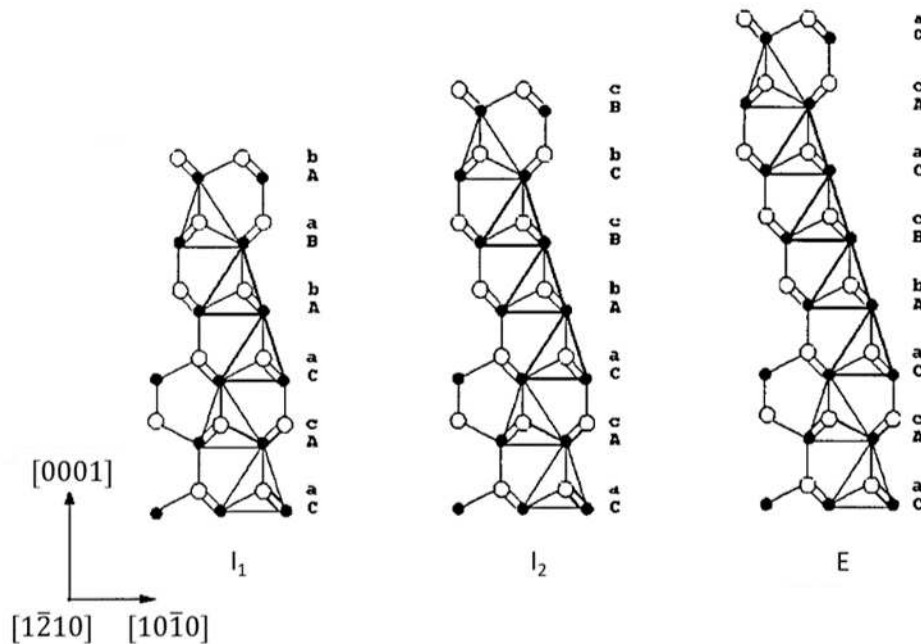


Figure 1. 5 Schematic representation of stacking fault I_1 , I_2 , and E present in wurtzite structures along the $\langle 11\bar{2}0 \rangle$ direction. Upper and lower case refers to cations and anions, respectively. Reproduced and adapted from Potin et. al. [51], DOI: <https://doi.org/10.1088/0953-8984/12/49/332>, with © IOP Publishing permission. All rights reserved.

1.2.2. Transition metal nitrides (TMNs)

Transition metal nitrides (TMNs) are a wide class of material that has been recently studied for different applications that span from hard coating to thermoelectric barriers and spintronic devices. This

broad range of applications is due to their exceptional combination of properties, such as refractory behaviour, high electron conductivity and chemical inertness.

Depending on the nature of the metal ion, these materials are usually stable in MX or M₂X or M₃X formulas, where M and X are the metal and non-metal ions, respectively. Early transition metals, such as Ti, W or Mo are usually found in MX or M₂X formulas, while later transition metals, such as Mn, Co, Ni, are more stable in M₃X compounds [52]. As shown in Figure 1.6, depending on the position of the metal in the periodic table, TMN materials can be stable in rock-salt fcc cubic (a), hexagonal close-packed (b) or simple hexagonal (c) structures [52], [53]. In addition, it is possible to estimate which structure is the most stable for any TMN using Hägg's rule: if the ratio r_x/r_m between the radius of the metal ion (r_m) and of the non-metal ion (r_x) is less than 0.59, then the material is stable in one of the simple structures illustrated in Figure 1.6. For instance, materials such as TiN, ScN, γ -MoN or β -W₂N respect this rule [53].

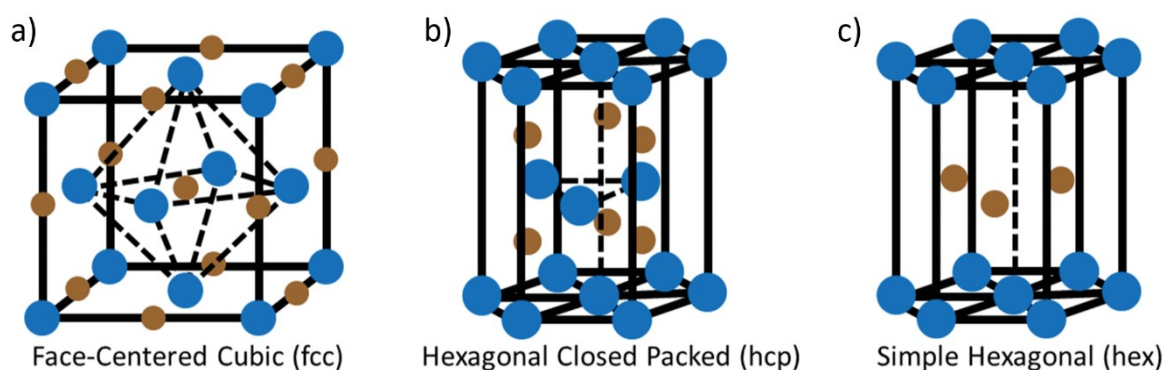


Figure 1.6 Schematic representation of the most common crystal structure of transition metal nitrides (TMNs): rock-salt face-centred cubic (a), hexagonal closed packed (b) and simple hexagonal (hex) structures. Reused and adapted from Zhong et al. [52], DOI: <https://doi.org/10.1002/advs.201500286>.

As mentioned above, TMNs are widely studied because of their interesting structural, electrical and magnetic properties. These properties arise from the unique coexistence of covalent, ionic and metallic bonds in the structure. The covalent contribution comes from the bond between the metal M and the non-metal X ions and the ionic bond is due to the charge-transfer between M and X, while the metallic contribution comes from the interaction between metal M ions [54]. Because of the coexistence of different types of bonds, TMN materials show the unique combination of ionic properties, such as high melting point, covalent properties, such as high brittleness and mechanical resistance, and transition metal material properties, such as high electron conductivity, magnetic susceptibility and catalytic behaviour [54].

However, depending on the nature of the M metal, the electronic properties of TMNs can vary. For example, early transition-metal TMNs based on group 4 and 5, such as TiN or VN, show metallic conductivity with resistivities ranging between 10 and 30 $\mu\Omega\text{cm}$ [55], [56]. In these TMNs, the metallic behaviour is related to the presence of electrons in the *d*-shell that are not involved in any bonds and,

therefore, are located in the antibonding states. These partially occupied antibonding states push the Fermi level into the conduction band, resulting in the metallic behaviour of the material. TMN materials based on group 3 or 6 metals, on the other hand, show semiconducting behaviour. In the first case, the 3 electrons in the d -shell are all involved in the bond with 2p valence electrons of N and the Fermi level drops into the band gap [56]. One example of 3-group TMNs is ScN that will be described in detail in the following section. In group 6 TMNs, instead, the semiconducting behaviour is due to the half-filled antibonding band $3d\ t_{2g}$. Electrons in these antibonding states cause the splitting of the band and, consequently, the drop of the Fermi level into the band gap [56]. Finally, regarding the electronic properties of later transition-metal TMNs, they all show metallic behaviour, with the exception of Cu_3N and Zn_3N_2 , which are known to be semiconductors [55].

1.2.2.1. ScGaN and ScAlN

Transition metal nitrides (TMNs) with formula $\text{Sc}_x\text{M}_{1-x}\text{N}$, where M is a 13-group elements Ga or Al, have also attracted increasing research attention for optoelectronic and energy harvesting applications, due to their optical, electrical and piezoelectric properties. The properties of TMN ScN and ternary ScGaN and ScAlN are summarised in this section.

Binary ScN

Binary ScN is a unique transition metal nitride that shows intermediate behaviour between metallic transition metal nitrides and semiconducting III-nitrides. At room temperature ScN is stable in rock-salt cubic structure, as most of binary TMNs, with space group $\text{Fm}\bar{3}\text{m}$ and lattice parameter a equal to $4.5057 \pm 0.0005\text{ \AA}$ [57]. In addition, similarly to GaN and AlN, ScN shows semiconducting behaviour with an indirect band gap of 0.9 eV ($\Gamma \rightarrow \text{X}$) and a direct band gap of 2.1 eV ($\text{X} \rightarrow \text{X}$) [58], [59]. This semiconducting behaviour arises from the electronic configuration of Sc: the shell structure of Sc is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ and, since the outmost $3d$ and $4s$ electrons are all involved in the Sc – N bond, no free d electrons are present in the structure. Hence, the Fermi level is pushed into the band gap leading to the semiconducting behaviour [21], [60].

As mentioned before, at room temperature ScN is stable in rock-salt cubic structure, however Takeuchi et al. [61] calculated the stability of other possible phases at room temperature, and found that the metastable wurtzite phase of ScN ($wz\text{-ScN}$) is less stable than the rock-salt phase ($rs\text{-ScN}$) of only 0.34 eV/formula unit. They also calculated that this $wz\text{-ScN}$ structure would have a band gap ranging between 4 and 5 eV and lattice parameters a and c equal to 3.49 $\text{\AA}$ and 5.58 $\text{\AA}$, respectively. Since these calculated lattice parameters are close to those of GaN and AlN (Table 1.3), they also suggested that alloying these III-nitrides with Sc in appropriate concentrations could stabilise the metastable wurtzite phase $wz\text{-ScN}$. Farrer and Bellaiche [62], on the other hand, calculated that $wz\text{-ScN}$ is unstable, and suggested a distorted hexagonal structure only 0.316 eV/formula unit more unstable than $rs\text{-ScN}$. In

this work, Farrer and Bellaiche have suggested that this metastable structure (B_k -ScN) consists of a distort wurtzite structure with lattice parameters a 3.66 Å and c 4.42 Å and internal parameter u as large as 0.5, as shown in Figure 1.7. This large internal parameter can be explained as a flattening of the wurtzite unit cell, in which Sc is nearly bonded to five N ions in a trigonal bipyramidal geometry. Such that, Sc and N ions lie in the same basal plane and the point space becomes 6/mmm, resulting in a non-polar structure.

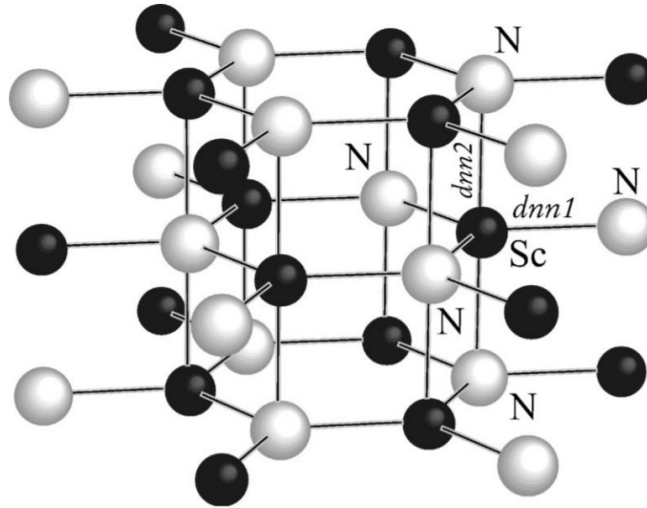


Figure 1. 7 Schematic representation of hexagonal wurtzite-like structure of ScN calculated. Reprinted Figure with permission from N. Farrer, L. Bellaiche Phys. Rev. B, 66 pp. 201203-201206 (2002) Copyright 2002 by the American Physical Society [62], DOI: <https://doi.org/10.1103/PhysRevB.66.201203>.

Ternary ScGaN and ScAlN

Although the metastable B_k – ScN structure has not been observed yet, Ferrer and Bellaiche predicted that it might be stabilised in alloy systems such as $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ and $\text{Sc}_x\text{Al}_{1-x}\text{N}$ [62], [63]. As described above, when Sc is introduced in GaN structure, all electrons in the Sc outmost shell are involved in the Sc – N bond. Therefore, no d electrons are present in the conduction band and the sp^3 hybridisation is maintained using minimal energetic stabilisation. This retention of the sp^3 hybridisation results in much higher solubility of Sc in both ScGaN and ScAlN, compared to other transition metals [21]. From theoretical results, in fact, Sc was found soluble in both GaN and AlN system for every composition and three different structures are predicted, depending on the final concentration of Sc in the system. As shown in Figure 1.8, the hexagonal wurtzite structure is expected to remain stable up to 66 % and 56 % of Sc in GaN and AlN systems, respectively; while for higher Sc concentrations, the rock-salt structure is the most stable structure [32]. In addition, when the concentration of Sc is increased from 0 to 66 % in GaN (or to 56 % in AlN), the wurtzite structure distorts with a gradual flattening of the wurtzite unit cell. Since the Sc – N bond is calculated to be slightly longer than Ga – N bond, an increment of both a and c parameters for higher concentration of Sc is expected. However, a increases

much faster than c with an overall reduction of c/a ratio from 1.6 to 1.2, which causes the flattening of the unit cell. When the c/a ratio becomes as low as 1.2 the transition from distorted wurtzite structure (B_4 -ScGaN) to a non-polar, layered wurtzite-like structure (B_k -ScGaN) is observed [32].

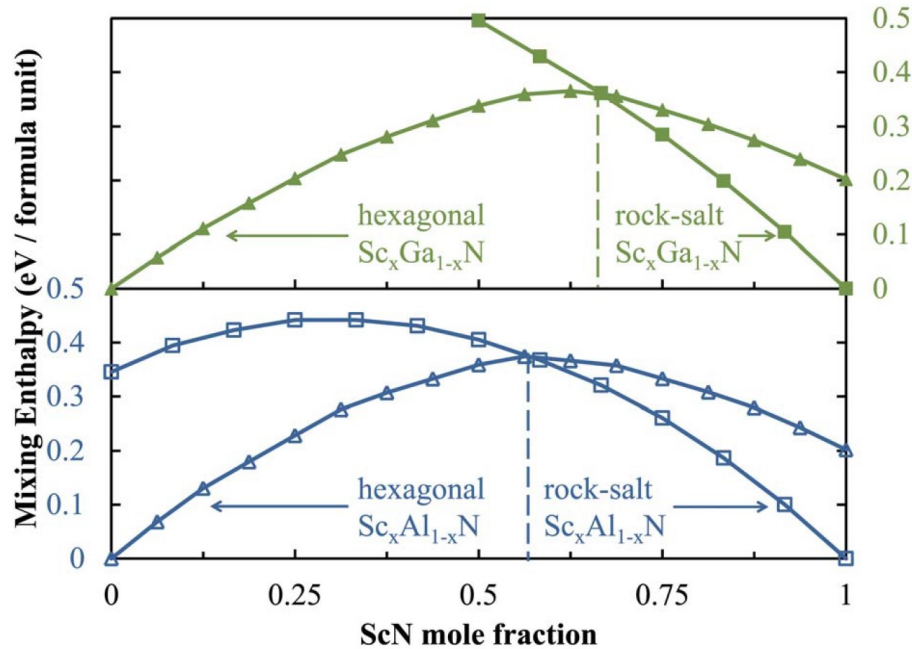


Figure 1. 8 Mixing enthalpy diagrams of ScGaN (green) and ScAlN (blue) for Sc concentration moving from 0 to 100 %. Reproduced from S. Zhang *et al.* [32] with AIP Publishing permission, DOI: <https://doi.org/10.1063/1.4824179>.

Although theoretical calculations have predicted that wz -ScGaN remains stable up to 66 % of Sc, experimentally spinodal decompositions in Sc-poor wurtzite and Sc-rich rock salts phases have been observed for much lower concentrations of Sc. Spinodal decomposition of unstrained ScGaN and ScAlN grown at 825 °C has been predicted at concentrations of Sc equal to 6 % and 11 %, respectively [32]. However, if compressive in-plane strain is taken into account, the wurtzite phase of ScGaN and ScAlN remains stable up to 27 % and 40 % of Sc, respectively [32].

The structural properties of ScGaN with different concentration of Sc have also been experimentally studied using HR-TEM analysis by Constantin and co-workers (Figure 1.9) [64]. From their experimental studies, they found that when the concentration of Sc is very low (up to 5 %) the ScGaN structure does not show any significant difference from GaN (Figure 1.9b). While, for higher concentrations of Sc (up to 17 %), high density of stacking faults is evident, and both ...ABAB... and ...ABCABC... stacking periodicities are observed (Figure 1.9c). A possible explanation of this high density of stacking faults might be that Sc tends to be stable in a 5-fold coordination of N atoms, while Ga is stable in a 4-fold coordination. Therefore, the formation of Sc – N bond results more likely than the formation of Ga – N bond, leading to structural defects.

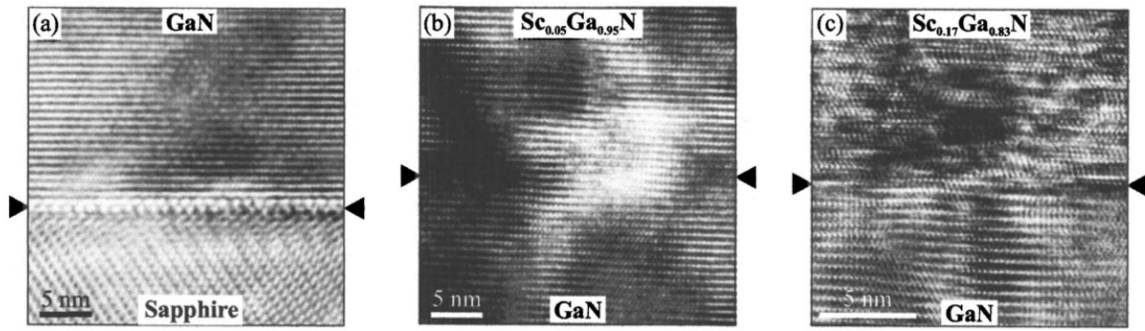


Figure 1.9 HR TEM images of GaN (a) and ScGaN with Sc concentration of 5 % (b) and 37 % (c). The increment of Sc concentration leads to generation of defects lowering the quality of the interface. Reprinted from Constantin et al. [64] with AIP Publishing permission, DOI: <https://doi.org/10.1063/1.2140889>.

The electrical properties of ScGaN and ScAlN have also been found to be strictly dependent on both the concentration of Sc and the experimental growth conditions. The calculated band gaps of ScGaN and ScAlN for different concentrations of Sc are shown in Figure 1.10: while in ScAlN the band gap decreases for higher concentrations of Sc, in ScGaN it is expected to increase up to 50 % of Sc concentration [21], [32].

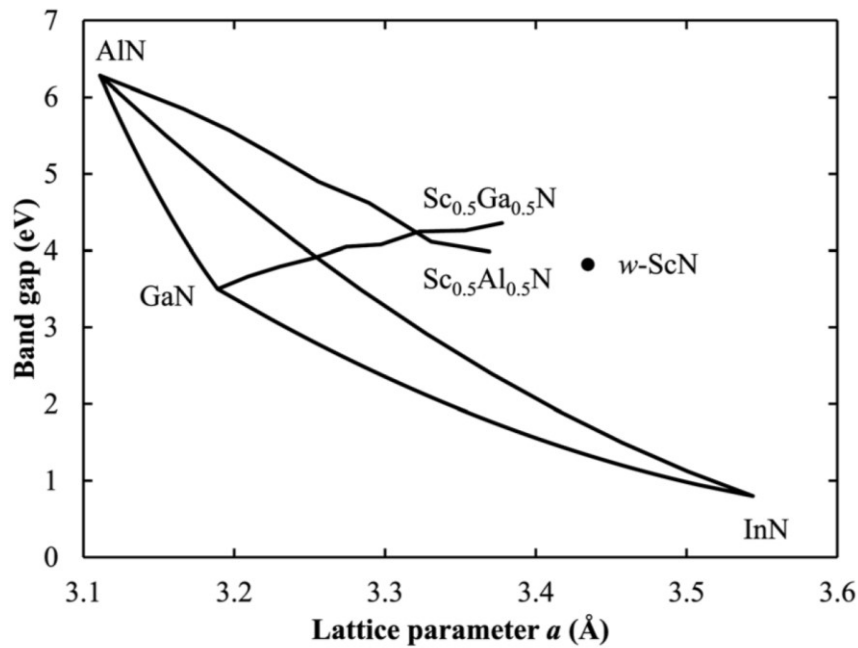


Figure 1.10 Expanded plot of variation of band gap and lattice parameter a with composition in ternary III-nitride materials. When Sc is introduced in AlN system the band gap decreases, while the lattice parameter a increases. When Sc is introduced in GaN both the lattice parameter a and the band gap increase. The calculated lattice parameter and band gap of wurtzite ScN (wz-ScN) is also shown. Reproduced from Zhang et al. [32] with AIP Publishing permission, DOI: <https://doi.org/10.1063/1.4824179>.

This different behaviour between ScGaN and ScAlN can be explained by studying the band structure of these materials. In Figure 1.11 the band structures of ScN, GaN, AlN and ScGaN and ScAlN, with Sc concentration equal to 12.5 and 25 %, are reported [32]. From this Figure it can be seen that in ScAlN the Sc states in the conduction band lie below the Al states. Therefore, when the scandium concentration

increases, the band gap decreases and remains direct up to 12.5 % of Sc. For higher concentrations, however, the valence band maximum (VBM) moves from Γ to M producing an indirect band gap $M \rightarrow \Gamma$. In the case of ScGa₃N₅, instead, the Sc states in the conduction band lie above the Ga ones. Therefore, when Sc is introduced in GaN system, both the effective mass and the high mobility of electrons remain nearly unchanged. In addition, it has been predicted that when Sc concentration changes from 0 to 50 %, the band gap increases from 3.4 eV (GaN) to 4.36 eV (Sc_{0.5}Ga_{0.5}N) and remains direct ($\Gamma \rightarrow \Gamma$) in the entire range of concentrations. Then, if the Sc concentration is pushed higher than 50 %, the band gap decreases down to the typical values of *rs*-ScN [32]. In addition, when Sc is introduced in both AlN and GaN systems, a large increase of number of states and flattening of the structure are visible in both the conduction and valence bands. Both these variations are believed to be related to the presence of Sc-states in III-nitride systems: the first is due to the localised nature of Sc-3d states, while the latter is attributable to the band splitting caused by the presence of Sc [32].

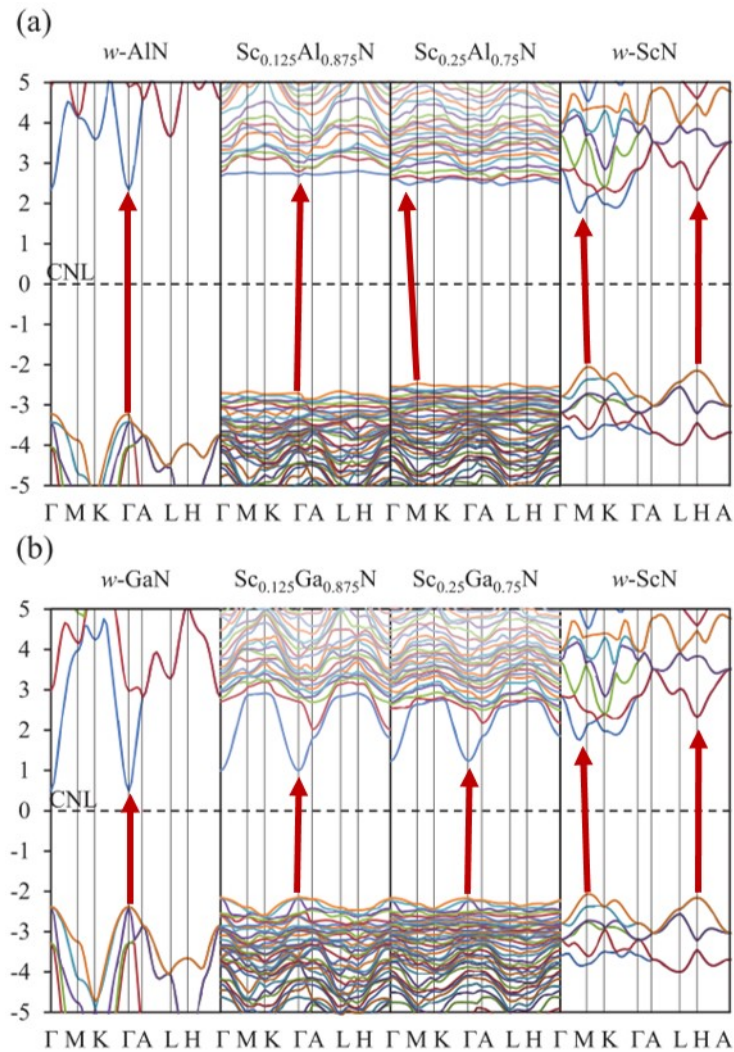


Figure 1. 11 Band structure calculated for binary AlN, ScAlN and ScN (a) and GaN, ScGa₃N₅ and ScN (b) with Sc concentration of 12.5 % and 25 %. The red arrows highlight the minimum conduction bands and the maximum valence bands of the materials. Reproduced from Zhang et al. [32] with AIP Publishing permission, DOI: <https://doi.org/10.1063/1.4824179>.

In addition, according to the values of the valence band maximums (VBM) and conduction band minimums (CBM), a large band offset is expected at both AlN/ScAlN and GaN/ScGaN interfaces. Moving from binary AlN to ScAlN, in fact, the VBM increases of slightly less than 1 eV, whereas CBM remains almost the same. In ScGaN case, the variation of VBM and CBM between GaN and ScGaN is few tens of eV and 1 eV, respectively. In addition, Tsui et al. [65] have found that when ScGaN is grown on the top of GaN, a type II heterojunction is obtained, in which only the VBM or the CBM of one material lies beyond the interface and within the other material. Because of this spatial separation, the recombination of carrier is slower than in type I heterojunction, this separation favours the generation of carriers in the 2DEG channel of the ScGaN-based HEMT [65]. Therefore, the width and nature of these band offsets make Sc-based alloys very interesting materials for application based on heterostructures such as LED and HEMT devices. However, experimental results do not always agree with these predictions. From experimental studies, it has been found that the band gap of ScGaN strictly depends on the quality of the thin films, and the presence of oxygen impurities and defects in the structure can cause a reduction of the band gap [66]–[68]. Therefore, high-quality ScGaN thin films are necessary to obtain the predicted larger band gap.

Finally, the elastic properties of ScGaN and ScAlN have been studied. Generally, hexagonal structures are described using five coefficients: C_{11} , C_{12} , C_{13} , C_{44} and C_{66} . In both ScGaN and ScAlN, it has been observed that when Sc concentration increases the elastic constants C_{11} , C_{44} and C_{66} decrease while C_{12} and C_{13} increase [46] and this variation is probably related to the different ionicity of Ga – N and Sc – N bonds. When N interacts with Sc instead of Ga, in fact, the electron density around N increases, leading to more ionic, longer and more distorted Sc – N bonds. Because of these distortions, in ScGaN and ScAlN the shear moduli reduce, and the overall structure becomes softer and more elastic [21], [46].

In addition, it has been proven that when Sc is introduced in GaN and AlN systems, the piezoelectric constant also increases hugely. Generally, the piezoelectric behaviour of wurtzite structures is described using the piezoelectric coefficient e_{33} . This coefficient e_{33} is obtained by two contributions: the *clamped ion* one, which indicates the tendency of an atom to maintain its coordinates, and the *intrinsic* one, which indicates the displacement of an atom from its original ideal position [69]. In Sc-III-nitride materials, the main component of e_{33} is the intrinsic one and N is the element that mostly contributes to it. For ScAlN, Tasnádi and collaborators [70] have reported an increase of e_{33} as large as 400 % when the Sc concentration is equal to 50 %. They claim that this huge increment is the result of two factors: first, the ionic potential around Sc ions is wider and less deep than Ga ions, resulting in an internal parameter u greatly sensitive to any applied electric potential or strain. Second, when Sc is introduced in AlN (or GaN) system, a distortion of the wurtzite structure is expected. Depending on the concentration of Sc, in fact, ScAlN (or ScGaN) can be stable in either polar distorted wurtzite structure (B_4 -ScGaN) or non-polar wurtzite-like structure (B_k -ScGaN). This instability of ScGaN between a polar

and non-polar structure appears to have great influence on the electrical and piezoelectric properties of the material, resulting in a very large e_{33} constant in Sc-III-nitrides [70].

Regarding the piezoelectric properties of ScGaN under stress, Alsaad and co-workers [71] have calculated the piezoelectric constants of ordered ScGaN under both compressive and tensile stress, when Sc concentration changes from 0 to 75 %. They found that for Sc concentrations up to 50 %, the polar distorted wurtzite structure (B_4 -ScGaN) is the favoured structure, and when compressive strain is applied to this structure, a large e_{33} constant is calculated, much larger than the value calculated as weighted average for the corresponding Sc composition. In addition, when Sc concentrations are larger than 50 %, ScGaN undergoes a transition phase from polar wurtzite structure to non-polar wurtzite-like structure (B_k -ScGaN) and the e_{33} constant becomes negligible, due to the non-polar nature of this structure. In addition, the behaviour of the ordered structure at Sc concentration equal to 50 % was studied, and a large increase of the piezoelectric constant e_{33} is observed, much larger than the one of $\text{Sc}_{0.25}\text{Ga}_{0.75}\text{N}$. This anomalous behaviour of $\text{Sc}_{0.5}\text{Ga}_{0.5}\text{N}$ is believed to be related to the transition between polar and non-polar structures that takes place at this Sc composition. In this work, Alsaad and collaborators calculated that when 2 % of compressive strain is applied, the piezoelectric coefficient e_{33} of $\text{Sc}_{0.5}\text{Ga}_{0.5}\text{N}$ is equal to 8.3 C/m², whereas when the strain is tensile and equal to 6.25 % e_{33} is 6.2 C/m² [71].

According to these calculations, Sc-III-nitride materials can have piezoelectric constants close to the values of ferroelectric perovskites. These impressive piezoelectric properties make these materials interesting not only for energy harvesting applications, but also for HEMT devices. As explained later in detail, in fact, in GaN-based HEMTs the carrier concentration in the 2DEG depends on the spontaneous and piezoelectric polarization of the active layer. Therefore, employing materials with piezoelectric constant as large as Sc-III-nitride materials might improve the carrier concentration of the 2DEG channel and, in turn, the performance of the device.

1.2.2.2. (Fe,Ga)N

As mentioned above, over the last few years special attention has been paid to ternary TMN materials with formula $\text{M}_x\text{M}'_{1-x}\text{N}$, where M is a transition metal and M' is a group-13 element (*i.e.* Al or Ga). In particular, TMN (Fe,Ga)N and (Mn,Ga)N, known as dilute magnetic semiconductors (DMSs), have been recently investigated for their ability to combine magnetic properties, such as high-temperature ferromagnetism, with the electric and structural properties of III-nitride semiconductors. An increasing number of studies [72]–[76], in fact, have suggested the possibility to use these materials in electronic devices in which the spins of electrons are used as additional degrees of freedom. In these type of devices, known as spintronic devices, the possibility to manipulate the spin of electrons would introduce new functionality and increase the amount of processable information [73].

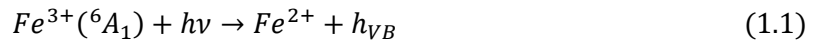
In DMS materials, such as (Fe,Ga)N, the magnetic transition metal ions (Fe) replace a small fraction of the cations of the matrix (Ga), inducing magnetic and ferromagnetic properties in the structure [77]. Generally, the wurtzite structure of binary GaN is built on the tetrahedral bond between Ga and N with hybridization sp^3 . Therefore, when the transition metal ions replace Ga in their sites, they have to contribute to this bond with three valence electrons. In the case of (Fe,Ga)N, Fe shell structure is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$, and it can contribute to the tetrahedral bonding with its d electrons, forming Fe^{3+} ions. However, since in GaN the Fermi level is very close to the conduction band, it is also possible that the third electron comes from a donor state and Fe contributes to the bond only with two electrons, in Fe^{2+} charge state. Both cases are possible and can coexist in (Fe,Ga)N [77], [78].

Regardless of the oxidation state, Fe d orbitals interact with N- p bands forming a tetrahedral bond with p - d hybridization. The presence of this p - d hybridization makes possible the spin interaction between the localized electrons of the magnetic transition metal and the free carriers in the GaN matrix, giving rising to ferromagnetic properties [77], [79]. The mechanism explaining the interaction between the electrons of the magnetic element and the free carriers is still under discussion and three potential mechanisms that can explain this interaction have been proposed, namely direct and indirect superexchange and double exchange [78]. In the first case the electrons in d orbitals of two neighbouring magnetic ions directly interact with each other, leading to an antiferromagnetic configuration. In the second case, the interaction between the d electrons of two magnetic ions is mediated by the free carriers of the matrix, usually leading to a ferromagnetic configuration. Finally, if the double exchange takes place, two magnetic ions stable in different charge states (*i.e.* Fe^{2+} and Fe^{3+}) can interact with each other via the hopping of one extra charge from one ion to the other. This latter mechanism is possible when the two neighbouring ions have same magnetic moments and the ferromagnetic configuration is favourite in this case [77].

(Fe,Ga)N and other DMS materials are predicted to show very high Curie temperature (T_C) and to retain their ferromagnetic behaviour near and above room temperature [72]. Although the T_C values and their relation to the transition metal concentration is still unclear and controversial for many DMSs, these materials are already of great interest for magnetic applications, such as spintronics.

In addition to these interesting magnetic properties, (Fe,Ga)N has also received great attention due to its electrical properties and semi-insulating behaviour [80]–[84]. In 1979 Monemar and Lagerstedt [85] studied the properties of GaN accidentally doped with small amount of iron and found that the presence of the transition metal impurities leads to insulating behaviour. Due to the possible application of these materials as substrate for GaN-based electronic devices, several studies have then been dedicated to the understanding of the role of iron in GaN-doped thin films [80], [83]. It is now clear that the iron impurities in (Fe,Ga)N introduce localized states right below the bottom of the conduction band which act as acceptor-like states. When iron is introduced in GaN matrix, it is usually stable in Fe^{3+} oxidation state with configuration d^5 . As shown in Figure 1.12a, when Fe^{3+} is in a tetrahedral crystal field of a wurtzite structure, its ground (^6S) and excited (^4G) states are transformed in $^6A_1$ and $^4T_1$, $^4T_2$, ^4E , $^4A_1$

respectively [78]. Using photoluminescence excitation (PL) experiments, Heitz and co-workers [86] characterized the luminescence transitions related to the iron impurities and they determined the position of the localized iron states within the band gap. In the PL spectra of all (Fe,Ga)N samples, a sharp peak, called zero-phonon line (ZPL), is observed at 1.299 eV, caused by the [${}^4T_1(G) - {}^6A_1(S)$] luminescence transition [78], [86]. This transition can be explained using the follow mechanism (Figure 1.12b): when (Fe,Ga)N is irradiated using photons with energy $h\nu$, a free photoelectron is generated in the semiconductor; $Fe_{Ga}^{3+}({}^6A_1)$ impurity then captures this photoelectron and generate the Fe_{Ga}^{2+} state and a hole in the valence band (1), according to Equation 1.1 [82], [86].



Then the hole and the Fe^{2+} recombines in a non-radiative manner leading to the excited state $Fe^{3+}({}^4T_1)$ (2). Finally, Fe^{3+} returns to the ground state ($Fe^{3+}({}^6A_1)$) via $d-d$ internal transition (3) that gives rise to the sharp ZPL line observed in PL [82]. From these PL experiments, Heitz and collaborators have been able to calculate the position of localized Fe^{3+} states at 3.17 eV above the top of the valence band and, therefore, only 0.34 eV below the bottom of the conduction band. Because of the close location of these states to the conduction band, these states act as acceptor-like states and are able to compensate the free carriers present in GaN, leading to semi-insulating behaviour [86]. Such that, typical resistivity of (Fe,Ga)N in the range of $10^9 - 10^{10} \Omega/\text{cm}$ is measured at room temperature [83].

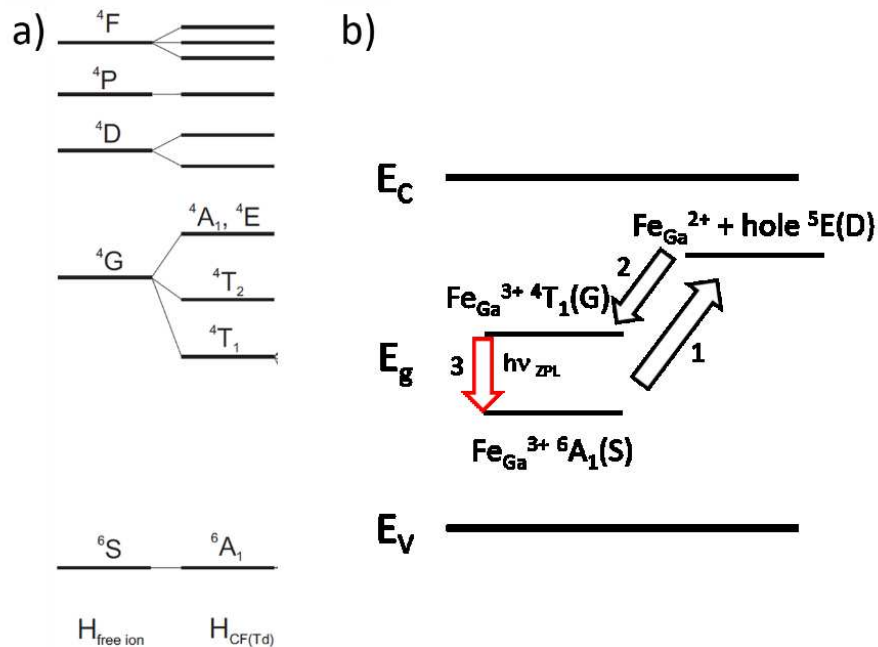


Figure 1. 12 a) Qualitative representation of Fe^{3+} states in the tetrahedral crystal field of wurtzite structure (reproduced and adapted from Malguth et al. [78], with John Wiley and Sons permission, DOI: <https://doi.org/10.1002/pssb.200743315>); b) schematic representation of the mechanism of [${}^4T_1(G) - {}^6A_1(S)$] luminescence transition (reproduced and adapted from Figure 2 in Dumcenco et al. [82], DOI: <https://doi.org/10.1063/1.3592343>).

These results are of great interest for optimization of GaN-based HEMT devices. When unintentionally doped GaN is grown in MOCVD or MBE systems, donor impurities, such as Si and O, are often incorporated in the thin films, lowering the performance of the device. This impurity often come from dirt or leakages present in the growth system, [87] therefore fine control of vacuum levels and evaporating temperature must be achieved to grow high-quality thin films. Introducing a semi-insulating layer, such as (Fe,Ga)N, between the substrate and the GaN layer should improve the insulation level of the device and, in turn, its final performance. However, the growth of high-quality (Fe,Ga)N is still very challenging, due to the low solubility of this transition metal in GaN structure. The solubility of first-row transition metals in GaN, in fact, usually varies between few percentages for (Fe,Ga)N [88] and about 7 % for (Mn,Ga)N [79] and depends on the conditions in which the film is grown. This low solubility of Fe and other transition metals in GaN is probably related to size mismatch between the transition metal and Ga and to electronic effects related to *d* electrons. At high concentrations, in fact, *d* electrons tend to occupy anti-bonding states, moving the Fermi level in the conduction band. The presence of the Fermi level in the conduction band results in metallic behaviour and consequent destabilization of the homogenous phase [21], [89]. Such that, while for concentrations of transition metal below the solubility limit the GaN structure remains unchanged [88], for concentrations above this limit, the generation of secondary phases and inclusions has been observed [88], [90].

The concentration of this secondary phase is generally very low and not-detectable using HR-XRD; hence, the study of these structures using transmission electron microscopy (TEM) imaging and energy dispersive X-ray spectroscopy (EDX) is now becoming mandatory to characterize accurately the properties of these materials [72]. Many studies have reported that (Fe,Ga)N thin films with concentrations of iron above the solubility limits show nanocrystal aggregations embedded in the GaN matrix, as illustrated in Figure 1.13a [88]. Using EDX analysis, it has been found that these aggregations are Fe-rich nanocrystals (Figure 1.13b) obtained from the precipitation of different phases, such as Fe_xN or (Ga,Fe)_xN [79], [88]. Similar results have been also observed for different TMNs such as (Mn,Ga)N [91] or MnGaAs [92], suggesting a general trend for this class of nitrides. The suggested mechanism for the generation of these nanocrystals is spinodal decomposition: when the concentration of Fe is higher than the solubility limit, the Fe ions in the GaN matrix tend to attract each other through attractive electromagnetic forces, leading to regions with high-concentration and low-concentration of transition metal within the GaN matrix [79].

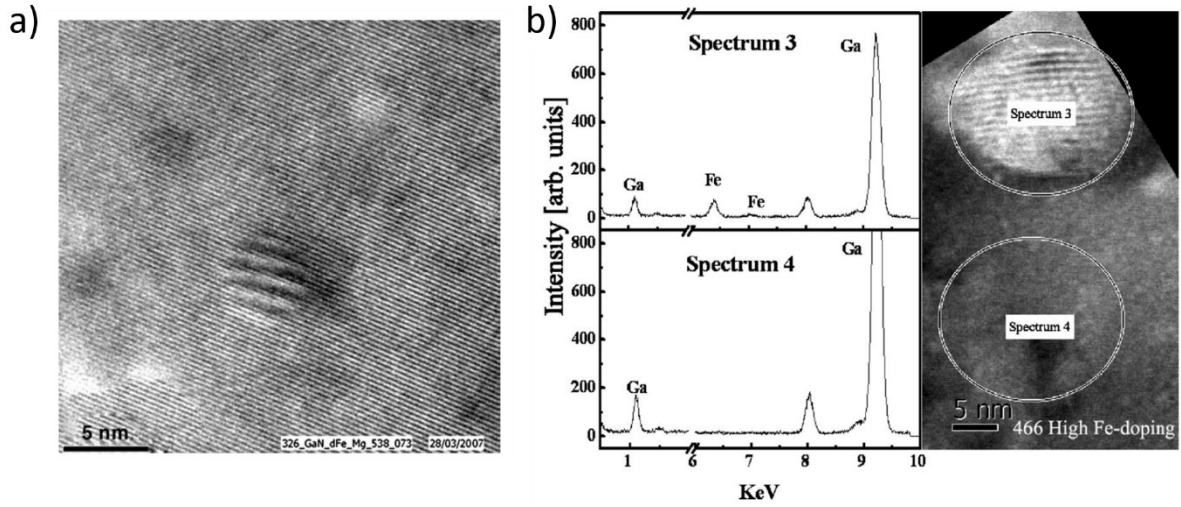


Figure 1. 13 HR-TEM image of (Ga,Fe)N nanocrystals embedded in GaN matrix (Reproduced Figure from Bonanni et al Phys. Rev. B, vol. 75, p. 125210 (2007) [79]. Copyright 2007 by the American Physical Society, DOI: <https://doi.org/10.1103/PhysRevB.75.125210>). b) EDS spectra of (Ga,Fe)N thin films taken around the nanocrystal (Spectrum 3) and in the GaN matrix (Spectrum 4) (Reproduced Figure from Bonanni et al Phys. Rev. B, vol. 75, p. 125210 (2007) [79]. Copyright 2007 by the American Physical Society, DOI: <https://doi.org/10.1103/PhysRevB.75.125210>).

The presence of these nanocrystals in the GaN matrix influences both the magnetic and electrical properties of the TMNs. An increasing number of studies, in fact, attribute the room-temperature ferromagnetism of these materials to the presence of these highly-concentrated nanocrystals embedded in the GaN matrix [79], [90]. The high concentration of the magnetic transition metal within the nanocrystal may give rise to superparamagnetism in the material with high blocking temperature. This type of magnetism generally appears in small ferromagnetic particles, such as these nanocrystals, in which the spin fluctuation is strictly dependent on the temperature. For temperatures lower than the blocking temperature, the spins within the nanocrystal are blocked, leading to ferromagnetic properties, while for temperatures higher than the blocking temperature, the spins fluctuate randomly so that the average magnetization is zero [93]. Therefore, it is possible that the high-temperature ferromagnetic properties observed in (Fe,Ga)N and related materials are due to the high blocking temperature of the spins in the superparamagnetic nanocrystals, which largely increases the overall T_C of the material.

In addition, it has been suggested that these nanocrystals play a crucial role in the electrical properties of these materials. Bonanni and co-workers [88] observed that when iron is introduced in GaN in concentrations lower than the solubility limit, the carrier concentration drops of about one order of magnitude (to 10^{15} cm^{-3}), leading to the expected semi-insulating behaviour. However, when the concentration of iron is higher than the solubility limit, and the nanocrystals are observed, the concentration of carriers increases up to 10^{18} cm^{-3} . While the first result is attributed to the well-known $\text{Fe}^{3+} - \text{Fe}^{2+}$ trapping mechanism, the latter result is still not completely clear. It is possible that is related to the inhomogeneous system caused by the presence of Fe-rich nanocrystals embedded in the GaN matrix, or that is somehow related to the electron hopping between highly-dense Fe ions. Other possible

explanations involve the presence of Fe ions in interstitial sites acting as double donors or the simple increase of oxygen impurities related to the faster ferrocene flux rates [88].

Therefore, to control the properties of the final material successfully and achieve the semi-insulating behaviour of (Fe,Ga)N, it is important to carefully monitor the concentration of iron during the growth. Because of the low solubility of transition metals in GaN, non-equilibrium growth techniques have become very popular for the growth of TMN-doped GaN materials [79]. The properties of (Fe,Ga)N grown using molecular beam epitaxy (MBE) [90], metalorganic chemical vapour deposition (MOCVD) [83] or Fe-ion implantation [94] have been reported, showing that magnetic and structural properties widely depend on the growth technique and conditions. An additional method used to increase the solubility of iron in GaN matrix and suppress the nanocrystal generation involves the use of co-dopants such as Si or Mg [95]. As explained earlier in this chapter, transition metal ions in the Ga substitutional sites act as traps for free electron carriers, leading to semi-insulating behaviour. However, the trapped electrons change the electronic state of the ions, giving rise to Columbian repulsions between transition metal ions. If Si or Mg are present in the system as co-dopants, they introduce shallow levels within the band gap that can compensate this Columbian repulsion and increase the maximum solubility of the transition metal in the homogenous phase [79].

1.3 Growth techniques

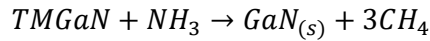
Since GaN and related nitrides have been proposed as promising materials for optical and electronic applications, great effort has been made to optimize the growth conditions of these thin films and improve their crystal quality. Currently, the most popular techniques used to grow III-nitrides and related materials are metalorganic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE). In addition to the growth of GaN, these techniques have been also used to grow transition metal nitrides (TMNs) with promising results. In this work, however, a different technique, known as electron-beam physical vapour deposition (e-beam PVD), has been chosen to grow the GaN and TMN thin films studied in this work. The working principles of these techniques, together with their advantages and disadvantages for the growth of TMNs, are described in the following sections.

1.3.1. Metalorganic chemical vapour deposition (MOCVD)

Since the mid-90s, metalorganic chemical vapour deposition (MOCVD) has been the leading growth technique for III-nitride materials. This technique, known also as metalorganic vapour phase epitaxy (MOVPE), has become popular because of its fine growth conditions monitoring, material flexibility, high growth rate (up to 5 $\mu\text{m}/\text{hour}$), high growth homogeneity (variations of the thickness less than 1 %) and potential large-scale upgrade. In MOCVD, the properties of the growing thin films are finely controlled by adjusting the substrate temperatures (typically between 1000 and 1100 $^{\circ}\text{C}$) and the III/V

materials ratios (typically between 10^4 and 10^5), and high-quality GaN thin films with dislocation density as low as 10^{-5} cm^{-2} have now been reported [96].

As the name suggests, in MOCVD the growth of GaN and other nitrides is obtained using metalorganic precursors as metallic source, such as trimetil-GaN (TMGa) or trietil-GaN (TEGa), while nitrogen is provided from an ammonia flow [97]. In the case of GaN growth, TMGa reacts with NH_3 in the growth chamber and the overall reaction is believed to be the following:



The mechanism of this reaction is yet not clear; however, a simplified representation is illustrated in Figure 1.14a. First the metalorganic precursors and NH_3 are introduced in the chamber (1). The metalorganic precursors are liquid at room temperature and are therefore introduced in the chamber using a carrier gas, typically nitrogen or hydrogen. Then the precursors can react in gas phase near the surface of the substrate (2). The intermediates obtained from these reactions then adsorb and diffuse on the surface (3). Finally, the intermediates can react and nucleate the final product (GaN) (4), while the volatile by-products are desorbed and pumped out of the system (5). This mechanism is common to other classes of chemical vapour depositions, however the precise steps of GaN mechanism are still under discussion [97]–[99].

Different types of MOCVD reactors are now available, however all of them share the same basic components. In Figure 1.14b a schematic representation of a Thomas Swan CCS reactor is shown as example [100]. In this system the metalorganic precursors and nitrogen are introduced using several closely-spaced tubes. The tubes give the advantage of reducing possible reactions between precursors before reaching the surface of the substrate and improving the quality of the thin film in terms of homogeneity and thickness-control. In addition, in this system the substrate is loaded on a susceptor that is heated at about 1000°C and rotated to improve the thickness homogeneity of the thin film. Since in these systems high temperatures are required to obtain high quality thin films, the entire reactor is usually contained in water-cooled chambers that maintain the temperature of the chamber under control. Finally, two exhaust tubes are used to remove volatile by-products.

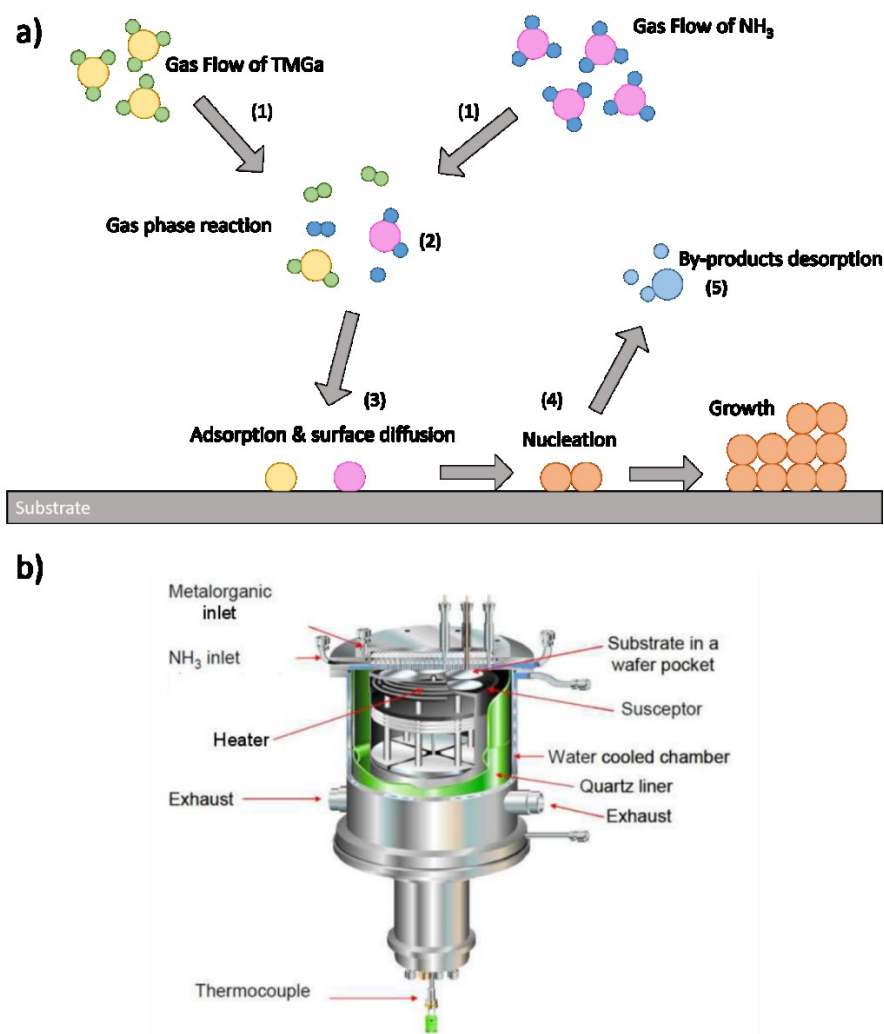


Figure 1. 14 a) Simplified representation of Growth mechanism of GaN thin film in a MOCVD system. In this representation the precursors (TMGa and NH₃) are introduced as gas flow using inert gas carriers (1). Once in the growth chamber they may first react in gas phase (2). The intermediate species then adsorb on the surface of the substrate (3) and react leading to the nucleation of GaN (4). Finally, volatile by-products are removed using exhaust tubes (5). b) schematic representation of a Thomas Swan CCS MOCVD reactor (reproduced from E.J. Thrush [100]).

In addition to the growth of GaN, this technique has also been recently used to grow transition metal nitrides such as (Fe,Ga)N and (Mn,Ga)N, however, one of the biggest challenges of using MOCVD to grow complex and alternative materials is finding suitable metalorganic precursors. In the case of (Fe,Ga)N and (Mn,Ga)N TMNs, the precursors usually used are Ferrocene (Cp₂Fe) and Manganocene (Cp₂Mn). As described in the previous section, when the concentration of the transition metal is above the maximum solubility limit, high concentrations of cluster were observed. Bonanni et al. [79] compared the properties of these materials grown both using MOCVD and plasma-assisted MBE and found that the MOCVD-TMNs show improved ferromagnetic properties when compared to similar MBE-TMNs. This improvement is believed to be related to lower concentration of defects and higher-crystal quality when MOCVD was used.

In the case of ScGaN, however, MOCVD is not suitable. Although growing ScGaN in MOCVD would make easier the integration with GaN and other nitride materials, no metalorganic precursor is currently available. Therefore, other growth techniques, such as MBE must be used to obtain ScGaN thin films.

1.3.2. Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) is a more recent growth technique mostly used to grow nitride thin films in research laboratories. However, over the past few years much effort has been devoted to make this technique industrially-relevant to produce GaN-based optoelectronic devices. Although the MBE technology is not yet as mature as MOCVD, using MBE to grow nitride thin films offers a number of advantages: lower growth temperature (600-800 °C), lower growth rates (up to 1 $\mu\text{m}/\text{hour}$), which improve the control of thin film thickness, rapid on/off switching of element sources, which improves the quality of complex heteroepitaxial structures, and in-situ monitoring of the crystal quality of the thin film using reflection high-energy electron diffractometer (RHEED) loaded in the chamber [101], [102].

In Figure 1.15 a schematic representation of an MBE system is illustrated. As in the MOCVD system, on one side of the chamber the substrate is loaded on a stage that can be heated and rotated during the growth. On the other side of the chamber, two or more guns are loaded with the precursors, which are thermally heated to obtain evaporation of the material. Each gun is also equipped with a shutter, so that the evaporation of the material can be rapidly interrupted and sharp interfaces obtained. In addition, in the middle of the chamber the RHEED system and a main shutter are also present.

The overall chamber is maintained in ultra-high vacuum (UHV) with pressures not above 10^{-9} torr [103]. Because of this low pressure, the main path free of the evaporated molecules is longer than the distance between the gun and the substrate, so that the evaporated molecule can reach the surface of the substrate unscattered. This unscattered path from the gun to the surface of the substrate makes possible the generation of a “molecular beam”.

Different types of MBE systems have been also proposed, depending on how the reactive nitrogen is introduced in the chamber. The most common systems are now the reactive-MBE [104] and the plasma assisted-MBE (PA-MBE). In the first case the nitrogen is provided by fluxing ammonia in the system, while in the second case the nitrogen is obtained using a radio-frequency (RF) [105] or electron cyclotron resonance (ECR) [106] plasma. Both these approaches have advantages and disadvantages: for instance, ammonia reacts more easily than molecular nitrogen (N_2), and thin films can be then grown at lower temperatures in reactive-MBE. On the other hand, it is very difficult to remove residual ammonia in the chamber after a growth, thus in reactive-MBE only nitrogen-rich conditions can be used. Furthermore, when ammonia is used, the oxygen incorporation is less likely than in PA-MBE, due to the reducing environment related to high concentration of ammonia; however, NH_3 is generally fluxed in the system using H_2 as carrier gas, which increases the hydrogen-incorporation in the final thin film [101].

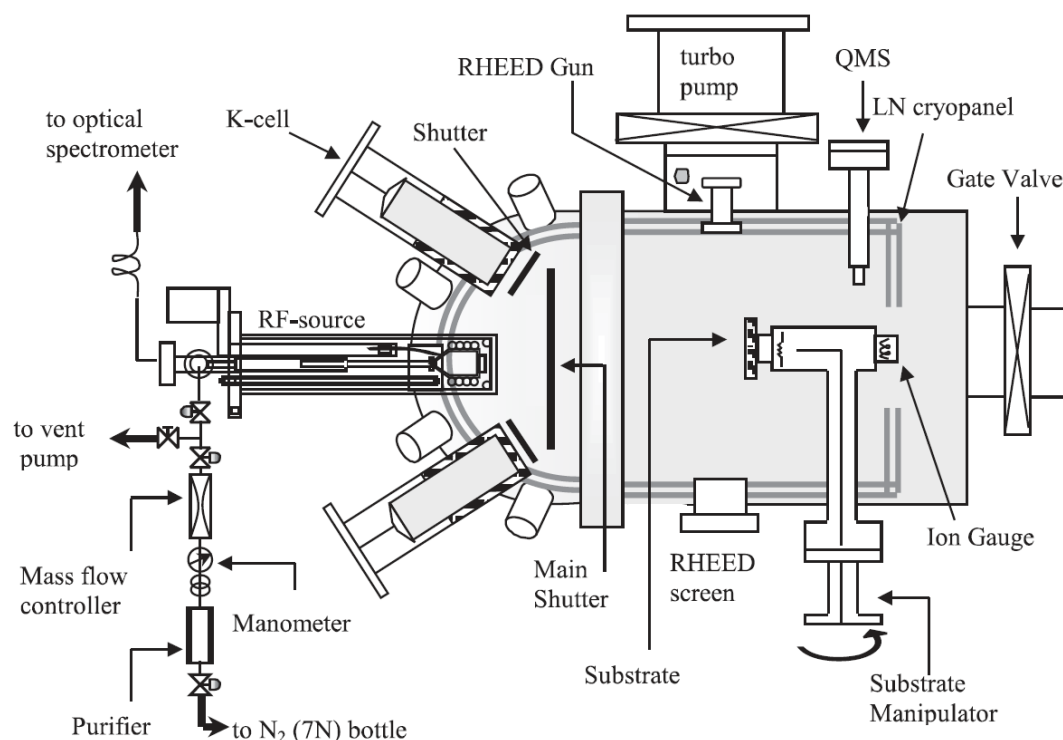


Figure 1. 15 Schematic representation of a molecular beam epitaxy (MBE) system. Reprinted from P. Ruterana et al., “Nitride Semiconductors: Handbook on Materials and Devices”, chapter 3, (2006), with the permission of John Wiley and Sons Publishing [101], DOI: <https://doi.org/10.1002/3527607641>.

The final properties of the thin films are strictly dependent on growth conditions such as III/V ratio in the chamber and the temperature of the substrate. Depending on the III/V ratio, the growth can take place in nitrogen-rich or metal-rich regimes and this regime influences not only the final composition of the thin film, but also its morphology and structural properties. In MBE systems, the III/V ratio can be modulated by changing the evaporation rate of the precursors and the partial nitrogen pressure (p_{N_2}). In addition, the III/V ratio depends on the sticking coefficients of the precursors and the properties of the surface where the growth takes place. In Figure 1.16 the growth regimes of GaN growth are reported as an example. In this case for very high III/V ratio, the nitrogen concentration is not sufficient to convert all Ga in GaN, and droplets of metallic Ga are observed. For intermediate III/V ratios the Ga-rich regime is achieved, while for very low III/V ratio the N-rich regime is obtained. In the case of GaN, the highest-quality of thin film is obtained using III/V ratios lying at the transition point between Ga- and N-rich regimes [107].

The set temperature of the substrate also has a great influence on the properties of the thin films. High temperatures are necessary to achieve rapid diffusion of the precursors adsorbed on the surface of the substrate, as well as to facilitate their decomposition and reaction. However, too high temperatures lead to rough surfaces, decomposition of the deposited thin film and desorption of precursors. Therefore, an optimal intermediate temperature must be found to obtain high-quality thin films. In the case of GaN and related materials this temperature usually varies between 600 °C and 800 °C [104].

MBE has also been widely used for the growth of transition metal nitrides. It has been found that when TMNs such as (Fe,Ga)N or (Mn,Ga)N are grown using MBE, the structural and magnetic properties, as well as the solubility limits of the transition metals, strictly depend on the III/V ratio used during the growth. For high III/V ratios, the growth rate of (Mn,Ga)N increases, while the maximum levels of Mn incorporations decrease [79]. In addition, a maximum solubility of Mn in GaN with Mn concentration as high as 6.3 % has been recently achieved using MBE [108].

Regarding ScGa₂N, MBE is currently the most popular technique to grow this transition metal nitride. This popularity is mainly because of the lack of metalorganic Sc precursor, that makes MOCVD unsuitable for the growth of this material. In addition, the structural properties of MBE-grown ScGa₂N have been found strictly dependent on the III/V ratio used during the growth. Knoll et al. [109] grew ScGa₂N using reactive-MBE and found that in N-rich conditions the nucleation of Sc inclusions is maintained under control. However, they also noticed that hot Sc may react with ammonia leading to the generation of unwanted, non-volatile by-products. These results suggested that the growth of ScGa₂N using PA-MBE might be advantageous over reactive-MBE.

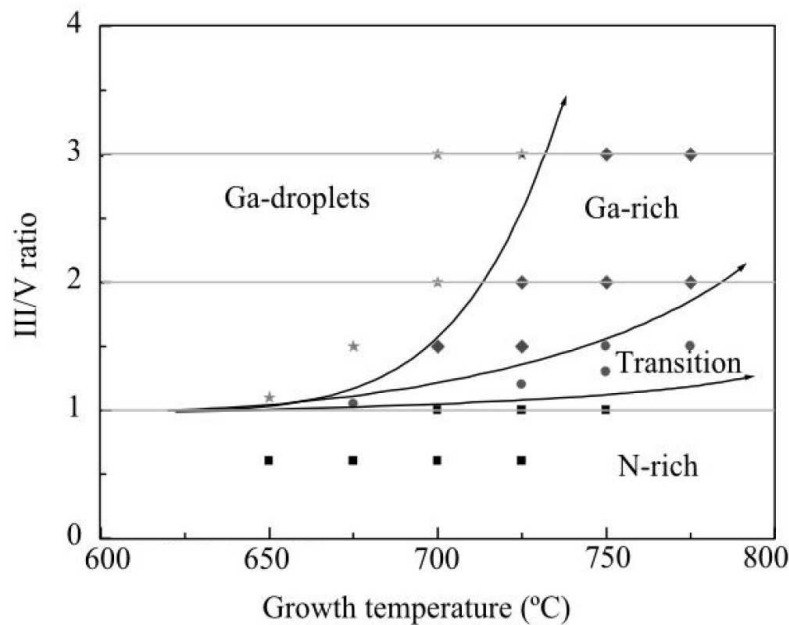


Figure 1. 16 Different growth regimes of GaN grown in PA-MBE obtained by using different III/V ratios and growth temperatures. Reprinted from H. Morkoç, "Handbook of Nitride Semiconductors and Devices: Materials Properties, Physics and Growth, Volume 1", Chapter 3, (2009), with the permission of John Wiley and Sons Publishing [107], DOI: <https://doi.org/10.1002/9783527628438>.

1.3.3. Electron-beam physical vapour deposition (e-beam PVD)

In addition to these two well-established growth techniques, in this work a third growth technique has been proposed to the growth of the transition metal nitrides under study. This third technique is electron-beam physical vapour deposition (e-beam PVD) and it has been used to grow all the materials reported in this thesis.

E-beam PVD has been widely used for the deposition of protective coatings, however very few studies have used this technique to grow nitride materials. Nevertheless, growing nitride materials using e-beam PVD may have a number of advantages, such as relatively high growth rate, large material flexibility and improved purity level of the thin films.

In Figure 1.17 three photos showing the main parts of the system used in this thesis are illustrated. As shown from the pictures, the e-beam PVD machine is made of a main chamber, where the growth takes place, three different e-beam guns, so that binary, ternary and quaternary nitrides can be easily grown and an RF plasma, which provides nitrogen. In addition, two loading chambers are attached, in which the substrate is annealed in vacuum before introducing it in the main chamber. This pre-treatment of the substrate is used to improve both the purity and vacuum levels of the system. Moreover, the RHEED detector or the Raman spectrometer can be used to carry out in situ characterisation of the growing thin film. Finally, a MANTIS software is used to choose the growth conditions and monitor the system, while windows can be used to visually control the growth and centre the e-beam on the surface of the target.

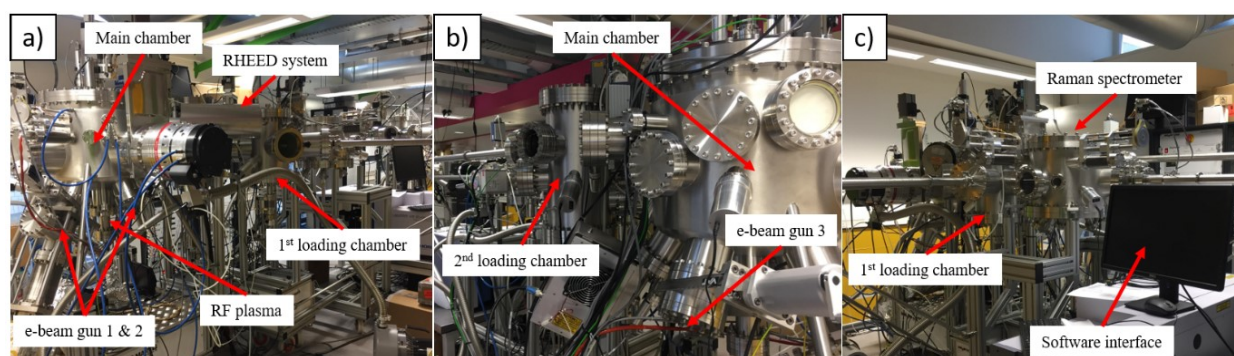


Figure 1. 17 Photographs of the e-beam PVD system in Imperial College London used for the thin film growth in this work.

In Figure 1.18a a schematic representation of the inside of the main chamber is also reported. As shown in this picture, after the substrate is thermally cleaned in the loading chambers, it is loaded to the substrate manipulator where it is heated and rotated during the growth. In addition, a pyrometer is used to monitor the surface temperature of the substrate. A mass spectrometer is also attached to monitor the nature and concentration of the reactants present near the surface of the substrate. Finally, shutters are mounted on the top of all e-beam guns and near the substrate manipulator, so that the deposition of the material in the gun can be rapidly interrupted and sharp interfaces obtained.

In Figure 1.18b the working principle of the e-beam PVD technique is also illustrated. The main components of this system are the tungsten filament (1), the deviating magnet (2), the sample crucible (3) and the substrate loader (4), as shown in Figure 1.17. The working principle of e-beam PVD can be explained as follows: an electron beam is thermionically generated by heating a filament of tungsten (1) and then deviated by a magnet (2) to hit the centre of the target in the crucible (3). The sublimated target material then diffuses in the main chamber reaching the heated substrate (4), which rotates at constant rate so that both the reaction rate and the homogeneity of the final film are enhanced. Since

the main chamber is maintained in ultra-high vacuum (UHV) ($10^{-9} - 10^{-11}$ torr), the particles impact directly on the heated substrate, so that any unwanted scattering event is avoided and the deposition rate ranges between 0.1 and 100 $\mu\text{m}/\text{min}$ [110], [111].

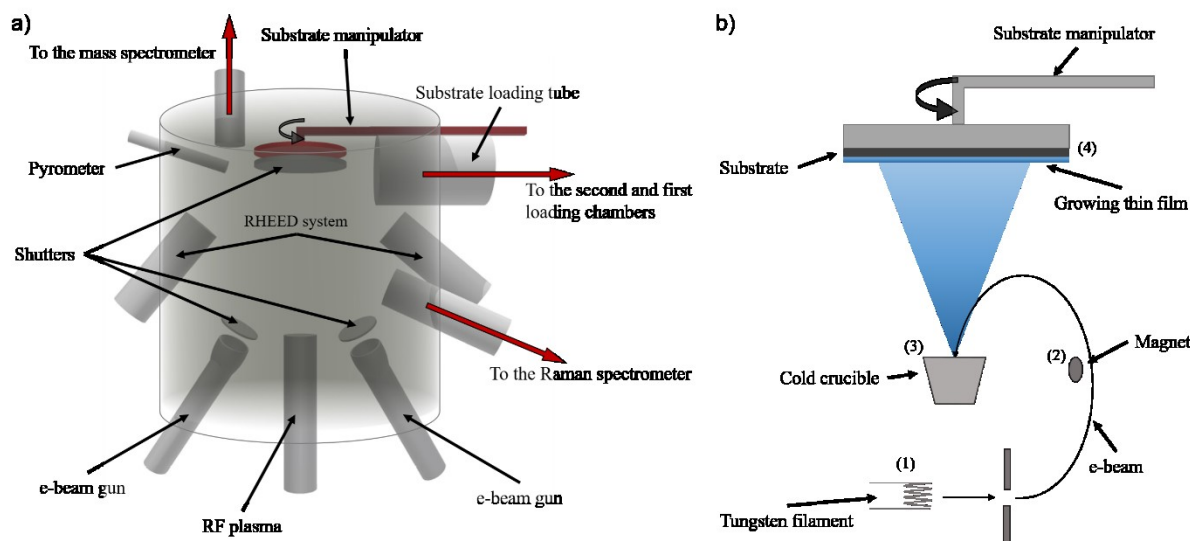


Figure 1.18 Schematic representation of the main chamber (a) and the working principle (b) of the electron-beam physical vapour deposition (e-beam PVD). The electron beam is generated by heating a tungsten of filament (1), then it is focused (2) to impact on the centre of the crucible (3). This impact causes the evaporation of particles of the target material that eventually reach the heated substrate (5) where they react.

One of the main advantages of this technique is the focused nature of the e-beam that interacts with the target. Since only a very small area of the target is heated, the temperatures achieved in that point are exceptionally high, while the rest of the crucible remains cold. This focused nature of the beam has a double advantage: first the crucible is cold during the growth, so that impurities and unwanted reactions are minimized; second, the local temperature on the heated spot can reach very high values, so that even thin films made of materials with high evaporation-temperature can be grown using e-beam PVD. Such that, after proper optimisation, e-beam PVD might be more convenient than both MOCVD and MBE for the growth of nitride materials. Compared to the MOCVD, e-beam PVD provides a much more flexible choice of target, since metallic precursor are used; while compared to MBE the area heated at high temperature is much more localised so that the impurity incorporation is maintained under control more easily.

If the e-beam PVD system is used to grow nitride materials, nitrogen is usually provided by using an RF plasma attached to the system. In the inductively coupled plasma high concentrations of nitrogen gas are dissociated in electrostatically-neutral nitrogen radicals; these reactive radicals are then introduced in the main chamber and react with other gas species and the substrate. The use of the RF plasma is particularly appropriate for epitaxial growth, since the radical will be highly reactive but not kinetically accelerated, and the damage to the grown film is minimized.

The properties of GaN, ScGaN and (Fe,Ga)N grown using e-beam PVD will be discussed in the following chapters.

1.4 High electron mobility transistor (HEMT)

1.4.1. HEMT working principle and 2D electron gas (2DEG)

As mentioned in the first section of this chapter, high electron mobility transistors (HEMTs) are a class of transistor in which the channel is generated at the interface of two semiconductor materials with different band gaps. As shown in Figure 1.19a, in nitride-based HEMTs a thin layer of AlGa_N, known as active layer, is usually grown on the top of a thick layer of Ga_N, the buffer layer. Since AlGa_N and Ga_N have different band gaps, at the interface a heterojunction is generated. The generation of this heterojunction can be understood by studying the bending of the band structure when AlGa_N and Ga_N are put in contact (Figure 1.19b). As illustrated in Figure 1.4, AlN has larger band gap than Ga_N, therefore AlGa_N has wider band gap than Ga_N and it increases when the Al content is increased. Because of the different band gaps, when the two materials are put into contact, a discontinuity at the interface arises and a triangular quantum well is obtained. As shown in Figure 1.19b, in fact, in AlGa_N/Ga_N heterojunctions, the bottom of this quantum well lies under the Fermi level and a 2D electron gas (2DEG) is formed [9], [23].

In HEMT devices based on other III-V semiconductors, such as GaAs, the high concentration of electrons is generally obtained by heavily doping the active layer, usually AlGaAs, with donor impurities, such as silicon. When doped-AlGaAs and GaAs are put in contact, the free electrons of the donor impurities are attracted in the quantum well and spatially confined in the 2DEG [112]. This spatial confinement improves the mobility of the electrons, hence the name high electron mobility transistors. However, the high concentrations of dopants in the active layer usually lead also to unwanted scattering and trapping events that lower the concentration and mobility of electrons in the channel. In contrast to GaAs-based transistors, the Ga_N-based ones do not need any doping of the active layer to achieve high concentration of electrons in the 2DEG channel. In the Ga_N case, in fact, the properties of the carriers in the channel of the transistors, such as velocity, concentration and mobility, mostly depend on the different polarizations of the active (AlGa_N) and the buffer (Ga_N) layers [23].

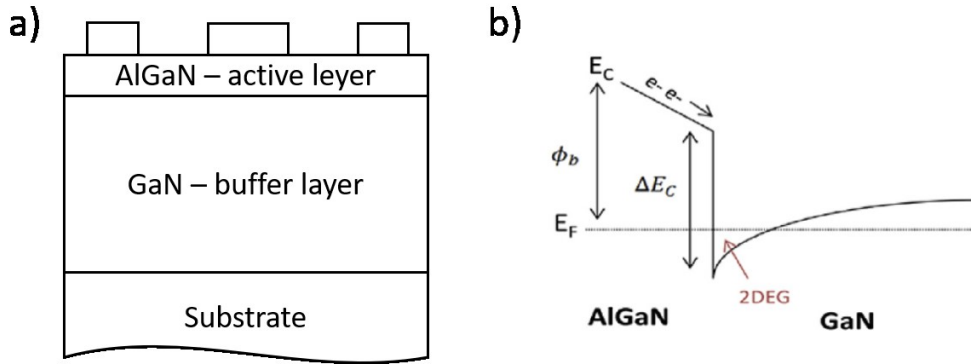


Figure 1.19 a) simplified representation of a GaN-based HEMT device. b) representation of the bending of band structure at the AlGaIn/GaN interface. The 2DEG lies below the Fermi level in these structures. Reprinted from *A survey of gallium nitride HEMT for RF and high power applications, Superlattice. Microsc.*, 109 (2017), pp. 519-537, A.S. Fletcher et al. Copyright (2017), with permission from Elsevier [9], DOI: <https://doi.org/10.1016/j.spmi.2017.05.042>.

As already described earlier in this chapter, GaN, AlN and their alloy AlGaIn are all stable in the polar wurtzite structure; however, all of them show some level of distortions along the c direction from the ideal structure, with c/a ratios lower than the ideal value 1.633 (Table 1.3). This distortion generates a certain level of spontaneous polarisation (P_{SP}) that is intrinsic of the material and is present without any external field. For III-nitride materials, the spontaneous polarisation increases when the distortion increases ($P_{GaN} < P_{AlGaIn} < P_{AlN}$) [113]. In addition, due to the polar nature of the wurtzite structure, a large piezoelectric polarisation (P_{PE}) also arises in these materials when maintained under strain [23]. In the case of AlGaIn/GaN HEMT heterostructure, the piezoelectric polarisation in GaN is negligible, since GaN is usually a few micrometres thick and therefore fully relaxed. On the other hand, AlGaIn is only 20-30 nm thick in HEMT structure; therefore, in the AlGaIn active layer the strained structure is favoured and a large piezoelectric polarisation arises. The magnitude of the piezoelectric polarisation in AlGaIn depends on the level of strain in the layer and, consequently, on the lattice mismatch between AlGaIn and GaN. In addition, since the spontaneous polarisation in AlGaIn is always tensile, if AlGaIn is grown on the top of GaN, it is under tensile strain and the piezoelectric and spontaneous polarisations can be added together. Consequently, in AlGaIn the overall polarisation is much larger than in GaN, and this difference generates a net sheet carrier density σ at the interface, as shown in Figure 1.20. The sign of this sheet carrier density depends on the polarity of the crystal and can be positive or negative if the crystal is Ga- or N- facing, respectively. To compensate this net sheet carrier density, free electrons in AlGaIn are attracted at the interface, lowering the bottom of the quantum well at the heterojunction well below the Fermi level [23]. Consequently, the 2DEG generated in this structure becomes highly populated. Finally, a negative sheet carrier density ($-\sigma$) is present at the AlGaIn surface to maintain the neutrality [114].

Therefore, it is evident that engineering the piezoelectric polarisation in AlGaIn layer is crucial to obtain high-performance HEMT devices. This polarisation depends on the composition of the layer: for higher concentrations of Al the lattice mismatch increases and, in turn, the level of strain increases.

However, for Al concentrations higher than 40 % the lattice mismatch between GaN and AlGa_N becomes too large. This large mismatch leads to generation of defects and roughening of the interface, which lower both mobility and concentrations of carrier in the 2DEG channel [23]. In addition, the value of the piezoelectric polarisation can be manipulated by changing the thickness of the active layer: using thicker AlGa_N layers usually leads to increased piezoelectric polarisations; however too thick layers tend to relax by generation of defects, making the piezoelectric polarisation negligible [114].

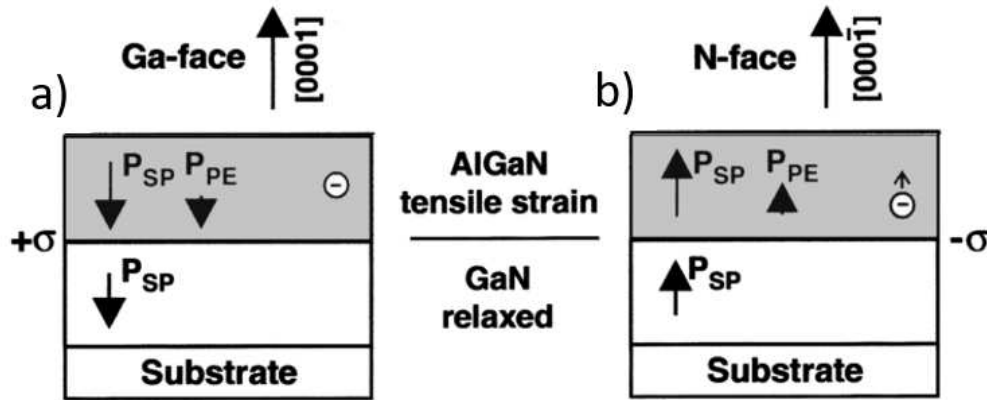


Figure 1.20 Schematic representation of spontaneous and piezoelectric polarisations present in AlGa_N and GaN in HEMT structures. Modified from S. Helkman et al. [23] with AIP permission, DOI: <https://doi.org/10.1063/1.1577222>.

1.4.2. Device operation and figure of merit

GaN-based HEMT devices are now used in different applications, such as high-frequency, high-power or switching applications. Depending on the final applications in which the device will be used, different figures of merit are considered to quantify the performance and the quality of the device. Nevertheless, regardless of the final application, all HEMT devices are characterized by the same basic structure, illustrated in Figure 1.2. In these devices, three contacts are always applied, namely source (S), drain (D) and gate (G). While the first two are usually Ohmic contacts, the last one has generally Schottky behaviour. In HEMT devices, the Ohmic contacts are generally obtained by growing a stack of titanium, aluminium, nickel and gold, followed by annealing to minimize the resistance at the interface with AlGa_N [115]. The Schottky contact, on the other hand, is made of a double layer of nickel and gold [116].

As described in the previous section, the 2DEG at the AlGa_N/GaN interface is generated due to the different polarisations of the two layers and, therefore, is present even when no external field is applied. Thus, if a voltage is applied between the source and the drain (V_{DS}), a certain current of electrons flows in the 2DEG channel, even if no voltage is applied at the gate contact. This class of devices is known as depletion-mode devices, and a negative gate voltage is required to pinch off the current in the channel [9]. Such that, if a positive voltage is applied at the drain contact, electrons start flowing in the channel

and the intensity of this current can be manipulated by changing the voltage applied at the gate contact (V_G). Depending on the applied voltage at the drain (V_{DS}) and at the gate (V_G), two different regions of operations can be identified. Figure 1.21 shows the current-voltage (IV) curves of a HEMT device when different gate voltages V_G are applied. For low V_{DS} , the current flowing in the channel increases linearly when the applied voltage increases, up to a point when the current in the channel is saturated and remains constant regardless of the V_{DS} applied. The voltage at which the current is saturated is known as V_{KNEE} and is strictly dependent on the gate voltage applied (V_G) and the concentration and mobility of electrons in the 2DEG channel. If the drain voltage is increased even further, the current abruptly increases and this voltage is known as breakdown voltage (V_{BR}).

Depending on the final application of the HEMT device, different contact geometries are used. For instance, in low-noise low-current applications, the intensity of the current in the 2DEG channel is greatly important and proportional to the gate width (W_G). Therefore, when HEMTs are used for this application, the width of the gate is much shorter than in power applications, where high concentrations of electrons flowing in the channel are necessary [117]. In high-frequency applications, on the other hand, the most crucial geometrical variable is the length of the gate (L_G) that must be as short as possible to enhance the maximum frequency of work (f_{max}).

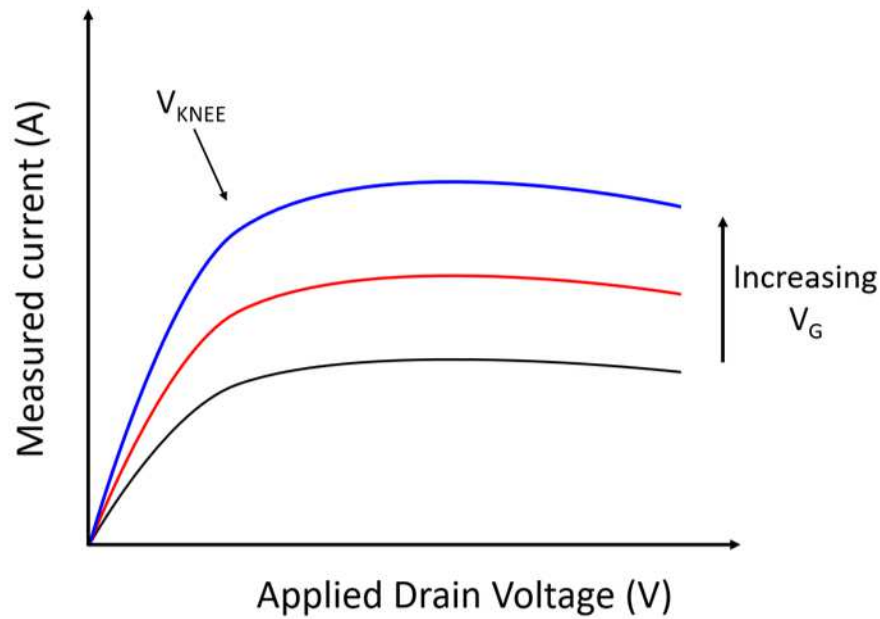


Figure 1. 21 Measured current (I) vs Applied voltage (V) of a generic HEMT transistor for different applied gate voltages.

Typical figures of merit used to define the quality of a HEMT device are the saturated current (I_D), the transconductance (g_m), power and power density, and the cut-off (f_T) and maximal oscillation (f_{max}) frequencies. In large-current, low-on-resistance applications, HEMT devices, loading a T-shaped gate 60 nm long, have shown drain current (I_D) as large as 2 A and transconductance (g_m) of 608 mS [118]. In addition, these devices have shown impressive output-power of 24.3 dbm at 3.2 GHz. In high-

frequency applications, GaN-based devices using a self-aligned gate 20 nm long have reported extremely high cut-off and maximal oscillation frequencies of 454 and 444 GHz, respectively [119]. In addition, it was found that when AlGa_N is substituted with AlN, as active layer, the cut-off frequency can increase up to 2.2 THz, with a low breakdown voltage [119]. Further data about the current performance and record figures of merit of GaN-based HEMT can be found both in the GaN 2018 roadmap [120] and in Fletcher's survey [9].

However, despite these astonishing results in a wide range of applications, the performance of GaN-based HEMT devices is still far from achieving their full potential and further investigations of device geometry and material properties are still necessary.

1.4.3. HEMT limitations

HEMT devices have already shown impressive results in different applications, however limitations in terms of material quality and device design still lower their performance. One of the biggest problems that limit the performance of these devices is the quality of the AlGa_N/GaN interface where the 2DEG channel is generated. As described in the previous section, because of the different polarisations between GaN and AlGa_N, high concentrations of electrons are accumulated and spatially confined at the interface, and accelerated in the 2DEG channel when drain voltage is applied [23]. However, the final concentration and the mobility of these carriers strictly depends on the crystal quality of the AlGa_N/GaN interface. To obtain high piezoelectric polarisation in AlGa_N thin film, and in turn high concentration of electrons in the channel, in fact, it is necessary that the AlGa_N layer is under high degree of strain [23]. However, this strain often leads to the generation of unwanted defects, such as dislocations, or cracking of the thin film. If high concentrations of defects or cracking are present in AlGa_N, these are believed to act as non-radiative recombination traps that lower the carrier concentration of the channel and, in turn, the performance of the device [27], [121].

Therefore, it might be of interest investigating alternative materials that could replace AlGa_N as active layer in HEMT structure. The use of an alternative material would in fact introduce a completely new set of piezoelectric polarisation/lattice parameter ratios that may lead to a high-quality interface and highly-dense 2DEG channel at the same time. In this sense, ScGa_N might be an interesting candidate, due to its large band gap and its large piezoelectric constant. If the HEMT device is based on a ScGa_N/GaN interface, the strain of ScGa_N necessary to obtain high piezoelectric polarisation would be relatively low, due to its large piezoelectric constant. This lower degree of strain of the active layer may, in turn, reduce the density of defects at the interface and improve the performance of the device. However, ScGa_N is still a relatively new material and many of its properties are yet under study. For this reason, one of the aim of this work is to investigate its structural, optical and electrical properties that might be of interest for future ScGa_N-based HEMT devices [21].

In addition to the quality of AlGa_N/Ga_N interface, another drawback that limits this class of device is the use of external substrates, such as Si or sapphire, on which to grow these materials. High-quality Ga_N substrates are still too expensive to be routinely used for the growth of Ga_N-based devices, therefore other cheaper substrates are usually employed. However, because of the lattice mismatch between these substrates and Ga_N, a certain density of threading dislocations and stacking fault are usually observed in Ga_N layer. Generally, this problem is solved by growing very thick Ga_N layer of the order of few μm .

Furthermore, donor impurities, such as Si or O, are usually introduced in the Ga_N buffer layer, generating a net background carrier concentration. This net background carrier concentration lowers the performance of the device, especially when they are used in high-power high-frequency applications [80], [83], [87]. It is expected, in fact, that the presence of a background current can lead to current collapse and lower the maximum frequencies at which the device can work [84]. One method to overcome this problem is by introducing an additional layer with semi-insulating properties between Ga_N and the substrate; semi-insulating materials such as Fe-, C- or Zn-doped Ga_N have already been proposed to overcome this problem. Among these materials, Fe-doped Ga_N appears to be the most promising, due to the acceptor-like states located right below the conduction band, which can compensate this net background current [84]. Lee and co-workers [87] have already studied the electrical properties of HEMT devices when an additional (Fe,Ga)_N layer is introduced between Ga_N and the substrate. They noticed that when (Fe,Ga)_N is used, the concentration of background carriers near the substrate is minimised, while the concentration of confined electron in the 2DEG is increased of about one order of magnitude.

However, the growth of this material is still very challenging, due to the low solubility of Fe in Ga_N thin film, and the crystal quality of (Fe,Ga)_N used in HEMT devices is often not clear in published work. Therefore, one of the aims of this work is to study the properties of (Fe,Ga)_N grown in different conditions and try to understand the relation between Fe concentration, structural properties and the semi-insulating and electrical properties of (Fe,Ga)_N thin film.

Chapter 2

Experimental techniques

2.1 Introduction

The following chapter will outline the theoretical principles of the techniques used to grow and characterize the thin films studied in this work. The comprehensive study of these materials can be classified in four different categories: study of influence of growth conditions on thin film properties and the characterisation of the structural, optical and electrical properties of the thin films under study.

2.2 Epitaxial Growth

Since the production of high quality, thick GaN substrates is still a very expensive process, GaN and related materials are usually grown on external substrates, such as sapphire, Si or SiC. However, because of the lattice mismatch between these substrates and GaN, certain degrees of strain are present in the nitride thin film. The strained film eventually relaxes by generating defects, such as misfit dislocations and stacking faults. To minimize the concentration of these defects, both the growth technique and the conditions in which the GaN growth is performed must be carefully chosen.

In this study all the thin films are grown using electron-beam physical vapour deposition (e-beam PVD) technique. The reasons of choosing this novel technique over the more popular MOCVD or MBE and the details of the e-beam PVD technique and system are described in Chapter 1.

All the thin films reported in this work are grown using a MANTIS plasma-assisted electron-beam physical vapour deposition (e-beam PVD) system. The thin films shown in this work were grown in similar conditions unless otherwise specified. Gallium 99.999 % pure, scandium 99.995 % pure and iron 99.99 %, purchased from Kurt J. Lesker and ILT Vacuum companies, were used as target; while nitrogen was provided using and RF plasma powered at 350W; finally, 0001-oriented sapphire was used as substrate. Before the growth, all the substrates were loaded in a first and second loading chambers, where the surfaces were cleaned by thermal treatment in vacuum. Then, the substrate is introduced in the main chamber where it is heated at temperature ranging between 750 and 850 °C depending on the specific growth. A pyrometer is used to finely measure the temperature on the surface of the substrate. Different e-beam currents were applied to the target, depending on the evaporating material and the final composition of the thin film. The specific values are reported in the following chapters. Similarly, the deposition time varied accordingly to the growth rate and the final thickness of the thin film. Full details of the growth conditions used in each Chapter are reported in Appendix A.

2.3 Structural and morphological characterisation

Structural and morphological properties, such as crystal-quality, defects or roughness, must be thoroughly investigated to fully characterize a thin film and understand the relation between the growth conditions and the crystal structure. In this work a range of microscopy techniques, such as atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-Ray diffraction (XRD) are used to investigate different properties of the thin films.

2.3.1 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a non-destructive technique widely-used to study surface properties of thin films. As illustrated in Figure 2.1, AFM is based on the interaction between the surface of the sample under study and a sharp silicon nitride tip, loaded at the edge of a flexible cantilever. When the tip is close to the surface, long-range forces, such as Van der Waals force, take place deflecting the cantilever. This deflection is detected using a laser beam pointed on the back of the cantilever and reflected to a photodetector, which converts the information into the final AFM image [122]. AFMs can work in three different modes, namely contact, non-contact and tapping modes. However, contact or non-contact mode are rarely used in semiconductor analysis, since in the first case both the tip and the surface can be likely damaged during the analysis, while in the second case the

resolution is generally too poor. AFMs working in tapping mode, on the other hand, can achieve high resolutions without risking damaging of the sample. In tapping mode, the cantilever oscillates at a chosen frequency close to the resonant frequency, and the AFM image is obtained by gently tapping the tip on the surface.

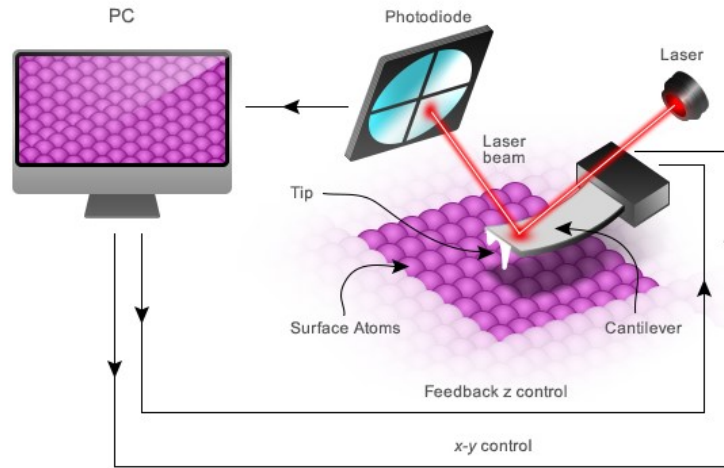


Figure 2. 1 Schematic representation of an AFM system used in tapping mode [123].

Because of the long-range interaction between the tip and the surface, if the surface morphology changes, both the amplitude and the frequency of the cantilever oscillation change accordingly. To correct this variation in frequency, a feedback circuit connected to the piezoelectric sample holder is used to maintain constant the distance between the tip and the sample by changing the sample height. This system is used to maintain the oscillation frequency of the cantilever close to the resonant frequency, according to Equation 2.1, and generate AFM images close to ideal conditions.

$$\omega = \omega_0 \left(1 - \frac{1}{k(dF/dz)} \right)^{1/2} \quad (2.1)$$

Where ω and ω_0 are the resonant frequency of the cantilever when the tip is close and far from the cantilever, respectively, k is the elastic constant of the cantilever and $\frac{dF}{dz}$ is the force gradient of interaction between tip and surface dependent on the distance [122].

Using AFM analysis, three types of image can be obtained, namely height, amplitude and phase images. The height image shows the morphology of the surface, and different contrast means different height on the surface; the phase image shows the homogeneity of the surface, and different contrast means different mechanical properties of the material on the surface; finally, amplitude image can show features on the surface and is usually used during the optimisation of the image acquisition.

Since its invention in 1986 [124], AFM microscopy has been a popular tool to study the properties of surface of thin films, as well as bio-materials and liquids. Its popularity is mainly due to the absence, or very little, sample preparation, its non-destructive nature, and to the high resolution that can be

achieved. Although the lateral resolution strictly depends on the radius of curvature of the tip and generally ranges between 10 and 40 nm, the vertical resolution can reach the sub-atomic level and mostly depends on the vibrational isolation of the instrument and the speed of response of the feedback circuit.

In this work, all the AFM images were acquired using a Bruker Innova AFM working in tapping mode. All images were obtained at room temperature at 1 Hz with 512 lines and processed using Gwyddion software [125].

2.3.2 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) is another non-destructive technique used to study the crystallographic properties of powders and thin films. To obtain an XRD diffractogram, an incident monochromatic X-ray beam is focused on the sample, where is elastically diffracted, and finally collected at the detector. The position and the width of the peaks in the diffractogram depend on the crystallographic properties of the sample and can be used to determinate the structure, the phase and the quality of the sample under study.

In order to interpret correctly the information in a XRD diffractogram, it is necessary to understand the concepts of direct and reciprocal spaces. The reciprocal space is a useful mathematical tool related to the Bravais reticules. The reciprocal space is described by the fundamental vector $\mathbf{t}^*$, calculated as the Fourier transform of the fundamental vector $\mathbf{t}$ of the direct space. Therefore, the fundamental reciprocal direction $\mathbf{a}^*$ is perpendicular to the vector product of the other two fundamental directions of the direct space $\mathbf{b}$ and $\mathbf{c}$ [126]. In addition, three fundamental equations (Equations 2.2-2.4), known as Laue's equations, can be used to describe the interaction of the incident beam with a crystalline sample and the difference of the beam path generated by this interaction.

$$\mathbf{a} \cdot \mathbf{K} = h \quad (2.2)$$

$$\mathbf{b} \cdot \mathbf{K} = k \quad (2.3)$$

$$\mathbf{c} \cdot \mathbf{K} = l \quad (2.4)$$

The scattering of the wave can also be either elastic or inelastic, depending on whether the magnitude of the reflected wave ($|\mathbf{k}|$) is equal to the magnitude of the incident beam ($|\mathbf{k}_0|$) or not.

In addition, Bragg's Law describe the specific case in which the reflected beam undergoes constructive interference generating a diffraction point. The constructive interference is obtained when the path difference between the incident and reflected beam is equal to $2d_{hkl}\sin\theta$, so that the Bragg's

Law is satisfied. As shown in Figure 2.2, d_{hkl} is the distance between the crystal planes, while θ is the incident and reflected angle.

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \quad (2.5)$$

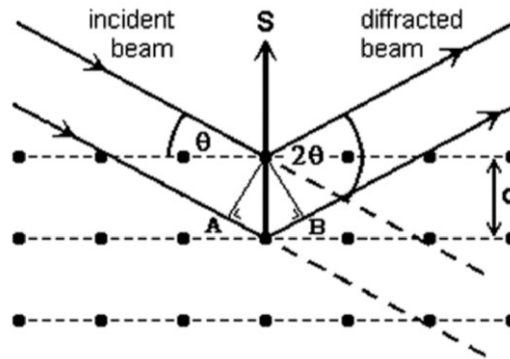


Figure 2. 2 Scheme of the conditions necessary to satisfy Bragg's law for a set of planes. Reprinted from Moram et al. [127], DOI: <https://doi.org/10.1088/0034-4885/72/3/036502>, © IOP Publishing. With permission. All rights reserved.

The indices hkl are known as Miller indices and are commonly used in crystallography to classify families of crystal planes and crystal directions. These indices can be defined as the intercepts of the crystal plane they describe with the fundamental directions $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ of the reciprocal lattice. Furthermore, a set of parallel crystal planes can be described using multiple Miller indices, i.e. (100), (200) etc.; however, since these planes are equivalent for transitional symmetry, they can be all described using the primitive ternary $\{100\}$. In addition, the Miller indices must be a triplet of integers, and they are calculated as the inverse of the intercept of the plane with the fundamental direct directions $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$; therefore, if the intercept is a fractional number, they must be multiplied by a common factor. Once both the Miller indices and the interplanar spacing d_{hkl} are known, the lattice parameters of both reciprocal and direct spaces can be calculated using the general Equation 2.6. However, if the symmetry constraints of the hexagonal crystal structure are applied, Equation 2.6 can be simplified in Equation 2.7. In this Equation both a and c are unknown, therefore two diffraction points, one symmetric and one asymmetric, are necessary to calculate the lattice parameters of hexagonal structure [127].

$$\frac{1}{d^2} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2kl b^* c^* \cos \alpha^* + 2hl a^* c^* \cos \beta^* + 2hk a^* b^* \cos \gamma^* \quad (2.6)$$

$$\frac{1}{d^2} = \frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2} \quad (2.7)$$

Components of the diffractometer

Since nitride semiconductors usually show high crystal quality, a high-resolution diffractometer (Figure 2.3) is generally used to study the crystal structure of these thin films. In a diffractometer, an

X-ray source is necessary, since the wavelength λ of the incident beam must be of the order of 1 Å to be able to resolve lattice distances.

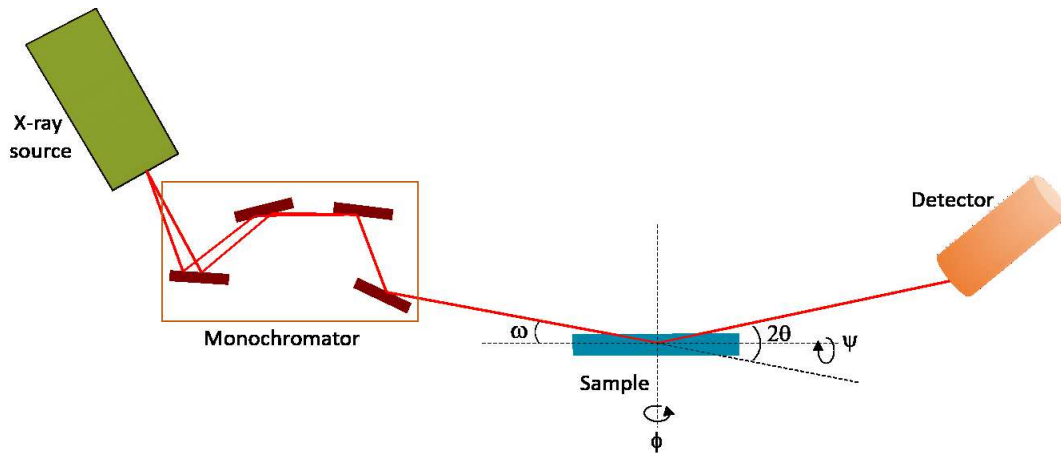


Figure 2. 3 Schematic illustration of an HR-XRD diffractometer used for thin film characterisation.

In a diffractometer the X-Ray source is a sealed X-ray tube. In the X-ray tube a copper target and a tungsten filament are used as anode and cathode, respectively. An electron beam is generated via thermionic effect by heating the filament and then accelerated onto the anode using a potential of several thousands of volts. When an accelerated electron strikes a copper atom, two effects are observed and shown in Figure 2.4 [127]. First most of the electrons are decelerated by the interaction with the nuclear core of copper atoms and generate a broad peak, known as Bremsstrahlung radiation. Second, electrons that are sufficiently energetic, hit the inner K shell of copper atoms and excite electrons within this shell, leaving a hole behind. This hole is then filled by a different electron falling from the nearest higher L shell. When falling at lower energy, this electron generates a photon with characteristic wavelength, which is equal to the energy difference of the two levels. Therefore, the wavelength emitted by the X-ray tube is strictly dependent on the anode material.

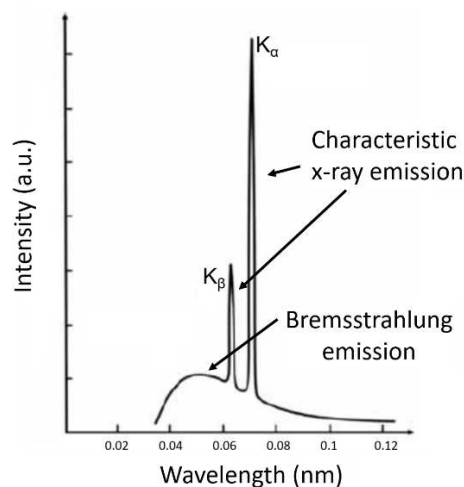


Figure 2. 4 X-ray spectrum showing the energy of electrons accelerated onto the copper anode. The sharp peaks are K_{α} and K_{β} , which are obtained by the falling of an electron from the L to the K shell of the copper atom. The underlying broad peak is the Bremsstrahlung radiation, due to the deceleration of electrons.

The most intense emission is K_{α} , however other emissions are also present, and a monochromator is usually necessary to remove any unwanted wavelength. To achieve the high resolution, a single crystal monochromator is usually used. This monochromator is generally an asymmetric 4-bounce Ge crystal, which is able to remove any unwanted wavelengths, such as K_{β} and $K_{\alpha 1}$ and to reduce the beam divergence δ as low as 0.003° [128]. The monochromatic beam then hits on the crystalline sample. As shown in Figure 2.3, the sample is usually loaded on an Eulerian goniometer that can translate along the directions x , y , z and tilt about ω , ϕ , ψ and 2θ .

Types of scan

The XRD analysis can be performed in different geometries depending on the type of information needed. The most common configuration is the 2θ – ω one: in this case, the sample is aligned so that the optimum ω angle is found, then the diffraction peaks are obtained by rotating the detector along the 2θ axis and the goniometer along the ω axis. Such that, while the detector rotate along 2θ , the Bragg law is satisfied only at specific 2θ angles and a peak is obtain at angles that strictly depend on the properties of the sample under study. This configuration is widely used to determine phase, preferential growth direction as well as the lattice parameters of thin films. The position of the 2θ peaks obtained using this configuration, in fact, depends on the nature of the material, their level of strain and lattice mismatch with the substrate underneath it.

In addition, the XRD analysis can be carried out also using ω , or rocking curve, configuration. This type of configuration is generally used to obtain information about the crystal quality and defect density of the thin film under study. In this configuration, the angle between the incident beam and the detector (2θ) is fixed at an angle that satisfies the Bragg Law for that film; then the sample rotates around the ω axis. To find the position of this ω angle for the thin film under study, a rapid 2θ – ω scan must first be performed. Then, finer alignment is necessary to refine the 2θ angle at which the scan is carried out. Once the optimal relative position of the detector and the sample holder is found, the sample is “rocked” around the set ω angle and a ω scan is registered. Such that, if the quality of the thin film is very high and virtually no misorientations are present, the Bragg law is satisfied only for a specific ω angle and the ω peak is very sharp. If misorientations and defects are present in the thin film, then the Bragg law is relaxed and partially satisfied for different angles near the set ω angle. This relaxation of Bragg law leads to a broadening of the ω peak, and the value of full-width-half-maximum of ω peak can be used as useful tool to estimate the crystal quality of thin films.

In this work, all samples have been analysed using a PANalytical MRD high-resolution diffractometer with a Cu K_{α} source equal to 1.5406 Å.

2.3.3 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a powerful technique used to analyse the structural, chemical and electrical properties of a thin film with extremely high resolution. Depending on the type of information needed, the TEM can be used in two different modes, namely diffraction and imaging modes. These different modes, their advantages and limitations are discussed in detail in this section.

Basic principles of Transmission electron microscopy (TEM)

In transmission electron microscopy the specimen is illuminated using a coherent parallel beam made of high-energy electrons accelerated from 100 to 400 kV. The use of electrons in TEM is necessary to be able to resolve crystal structure at the atomic level: according to the Rayleigh criterion the smallest distance that can be resolved using a microscope is proportional to the wavelength of the radiation used. So that, an optical microscope with a wavelength of about 550 nm cannot resolve object smaller than 300 nm. On the other hand, electrons with energy around 100 keV have a wavelength of the order of 0.005nm and it decreases for higher electron energies. The high resolution achievable is one of the feature that makes TEM one of the most powerful technique for semiconductor characterisation [129].

When the coherent electron beam interacts with the sample, the electrons interact with the atoms of the specimen and different phenomena can happen, as shown in Figure 2.5. After travelling through the specimen, the electrons can be transmitted (direct beam) or scattered, either elastically or inelastically, and either coherently or incoherently [129].

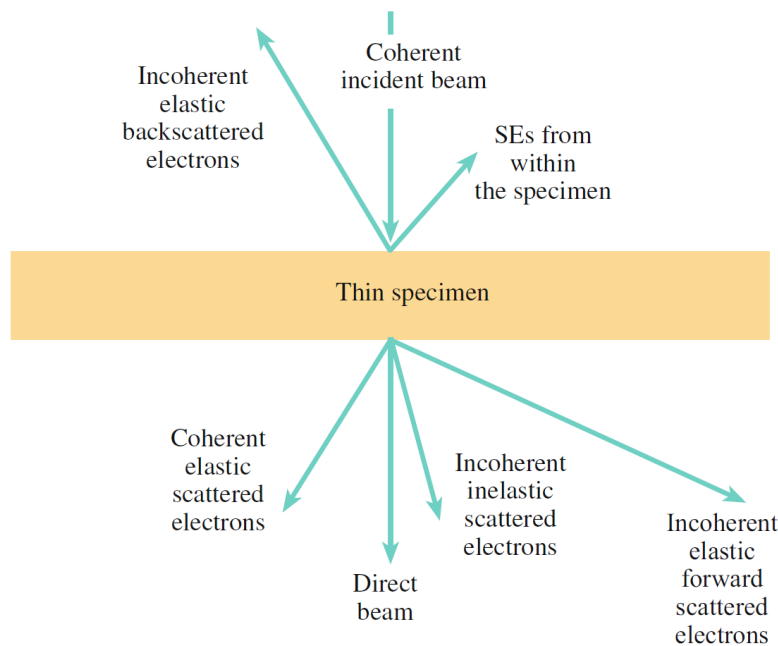


Figure 2. 5 Representation of the scattering events that can happen in the TEM when the electron beam interacts with the specimen. Reprinted by permission from Springer: Springer Nature, "Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 3 Scattering and diffraction" by D.B. Williams, C.B. Carter, (2009) Copyright. With permission of Springer Publishing. DOI: <https://link.springer.com/book/10.1007/978-0-387-76501-3> [129].

As a result, the emerging electrons have a nonuniform distribution of energy and angle and in this non-uniformity lies the information about the specimen under study. In TEM, the angular distribution of the emerging electrons can be used to obtain the diffraction pattern, while the spatial distribution of the emerging electrons can be viewed as contrast in direct images of the specimen, as described later.

Components of the Transmission electron microscope (TEM)

Similarly to the optical microscope, the TEM can be divided in 4 main parts: the source, the illumination system, the stage and the projection system. In Figure 2.6 a scheme of the TEM is shown.

The electron beam is generated using an electron gun as source (1). The electron guns commonly used in TEM are either thermionic guns or field emission guns (FEG). In the first case the electrons are obtained via thermionic effect by heating a sharp tip of LaB₆ or a filament of tungsten. In the second case a high electric field is applied to a tip of tungsten and the electrons are emitted via tunnelling phenomenon. The latter has recently become very popular, since it generates electron beams far brighter, more coherent and with smaller probe size than the thermionic sources [129]. The electron beam is then manipulated by the condenser lenses and apertures in the illumination system (2). First a condenser aperture is used to choose which fraction of beam interacts with the specimen: the smaller the condenser aperture the higher is the final resolution, however it will be at the cost of illumination intensity. Then, the electron beam is focused using a set of condenser lenses. After interacting with the specimen (3), the emerging electrons interact with the objective aperture and lenses (4). This set of lenses generates the first intermediate image of the specimen in the image-plane and a diffraction pattern in the back-focal plane. Finally, either the diffraction pattern or the image is magnified and projected on the phosphor screen (7) by the intermediate (5) and projector (6) lenses [129].

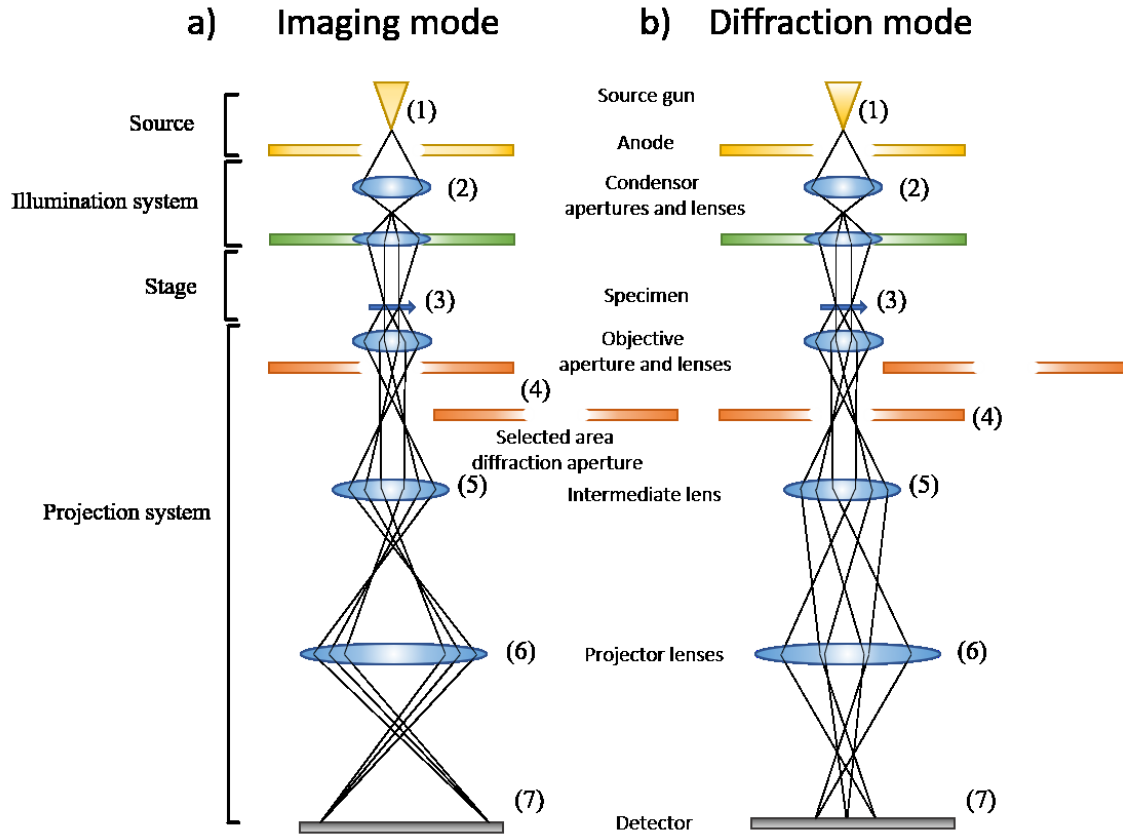


Figure 2. 6 Schematic representation of the component of a TEM used in imaging (a) and diffraction (b) modes.

In a TEM, the electron beam is focused using electromagnetic lenses: these lenses are made of a copper coil through which strong currents pass generating electromagnetic fields. Because of the interaction with these electromagnetic fields, the electrons in the beam move in a spiral path along the optical axis. When the current intensity is changed, the electron trajectories are deviated, and the electron beam is more or less strongly focused onto the specimen. However, due to the non-perfect cylindric symmetry of the coils and the defects in the microstructure of the copper, these electromagnetic fields are not perfectly uniform, causing deviation of electrons from the ideal spiral path. This deviation generates distortions in the final TEM images, such as astigmatism. These distortions are usually corrected using stigmators-correctors, which are able to generate electromagnetic fields that compensate the non-uniformity of the lenses [129].

Diffraction mode in TEM

As shown in Figure 2.6b, depending on the intermediate lens, the TEM can be used either in diffraction or imaging mode. When the TEM is used in diffraction mode, the emerging electrons will generate a diffraction pattern from which several bits of information can be obtained, such as phase, homogeneity and lattice parameters of the specimen. Since the specimen must be thin enough to be electron-transparent, the reciprocal lattice points often appear as elongated rod, known as relrods [129]. As shown in Figure 2.7, due to the elongated shape of these lattice points, more lattice points can

intercept the Ewald sphere and more diffraction spots are formed. However, the Bragg's Law is completely satisfied only by the lattice points that intercept the Ewald sphere in the middle, while the rest of the points satisfy the Bragg's Law only partially. The distance from the ideal Bragg's conditions determines the intensity of the diffraction spots and can be quantified using the excitation error s defined in Equation 2.8 [129].

$$K = g + s \quad (2.8)$$

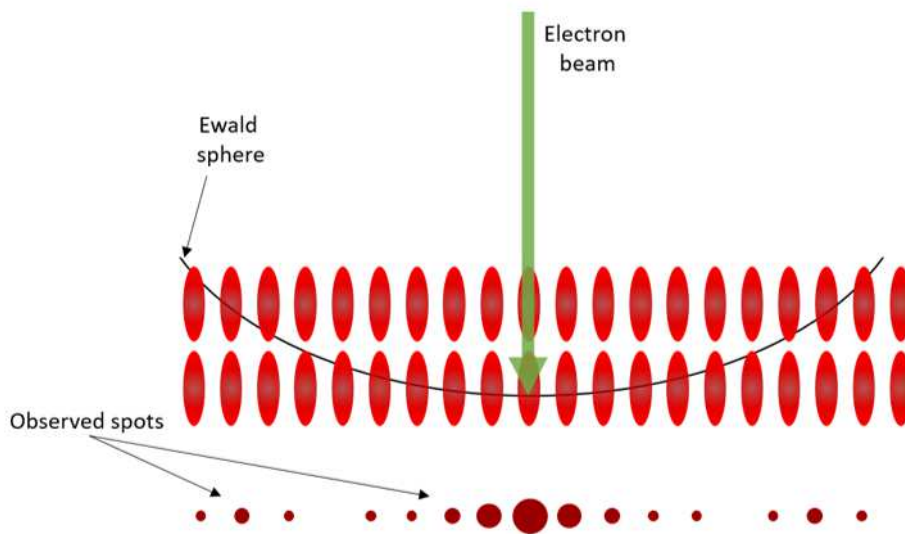


Figure 2. 7 Section of the reciprocal space in which part of the Ewald sphere and two rows of lattice relrods are shown. Only the relrods that intercept the Ewald sphere give rise to diffraction spots with different intensities.

However, compared to XRD, in TEM experiments electrons often undergo double or multiple diffraction, so that the intensities of the diffraction spots are not reliable for either quantitative and qualitative analysis. In addition, since the radius of the Ewald sphere is equal to $1/\lambda$ by construction, in TEM the Ewald sphere is much larger than in X-ray diffraction. Therefore, in electron diffraction a larger number of reciprocal lattice points intercepts the sphere and a diffraction pattern can be obtained without rotating the sample.

A complete diffraction pattern can be used to calculate the lattice parameters a and c and their ratio c/a , by measuring the distance between two diffraction spots. However, the precision of the calculated lattice parameters is much lower than that obtained using XRD. This reduced precision is due to the short wavelength of the electrons that leads to low scattering angles.

Imaging mode in TEM

If used in imaging mode, TEM can be used to directly “see” the crystal structure of the sample at magnifications ranging between 1 and 5 million times, depending on the quality of the microscope and

the alignment. As shown in Figure 2.6a, the imaging mode is obtained by introducing a small objective aperture and modulate the strength of the intermediate lenses.

Depending on the kind of information required, different type of images can be acquired, such as bright-field (BF), dark-field (DF) or high-resolution (HR). Bright and dark field images are complementary images obtained by selecting only the direct or one diffracted beam, respectively, while all the other beams are blanked. In fact, if no beam is selected, the final TEM image is generated by multiple diffracted beams and it will be very difficult to interpret. In BF and DF images, instead, the selection of one specific beam enhances the contrast of defects, such as dislocations or stacking fault, so that they can be more easily observed and studied [129]. In Figure 2.8 BF and DF images of GaN thin films are shown.

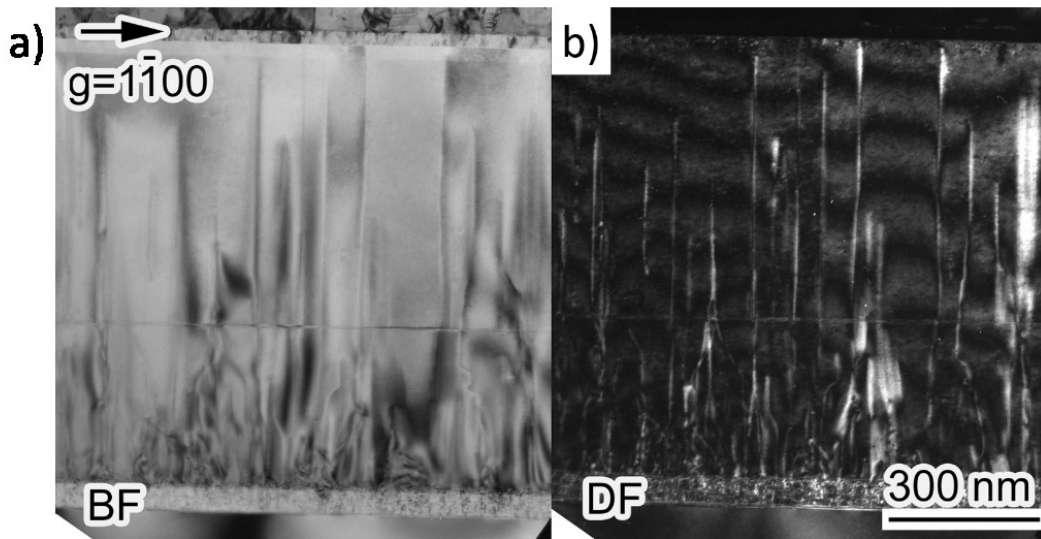


Figure 2. 8 Cross-sectional TEM bright-field (a) and dark-field (b) images close to the $[11\bar{2}0]$ zone axis of GaN thin film. Reused from Wong et al. [130] with AIP permission, DOI: <https://doi.org/10.1063/1.3009669>.

In HR imaging, instead, larger objective apertures, usually 50 μm large, are used to select the direct beam and few other beams diffracted in known directions. These selected beams interfere between each other generating the phase-contrast in the HR-TEM images. If the interference between only the direct and one diffracted beam is considered, the simplified Equation 2.9 can be used to calculate the intensity of the HR image:

$$I = A^2 + B^2 - 2AB \sin(2\pi(g + s)x - \pi st) \quad (2.9)$$

Where A and B are constants, s is the excitation error and t is the thickness of the specimen. According to Equation 2.9, in HR images the intensity is obtained as a sum of a smooth intensity ($A^2 + B^2$) and the interference of a sinusoidal periodic function with period $\frac{1}{(g+s)}$. If s is equal to 0, then the Bragg conditions are satisfied and the periodicity of the intensity of the lattice fringes coincides with $\frac{1}{g}$. So

that, when the Bragg conditions are satisfied, this periodicity can be used to obtain the value of the lattice plane spacing d_{hkl} using the relation:

$$d_{hkl} = \frac{1}{g_{hkl}} \quad (2.10)$$

When an objective aperture is inserted, the selected diffracted spots generate lattice fringes from which HR images are obtained (Figure 2.9). Thus, in the HR image the bright spots are not actual atoms, but maxima intensity generated by the crossing of these lattice fringes. However, even if the image is not a direct picture of the atomic structure, it can still be used to obtain lattice information. Due to the direct relation between fringes and selected diffracted spot, in fact, the distance between bright spots can be used to obtain d_{hkl} , as shown in Figure 2.9.

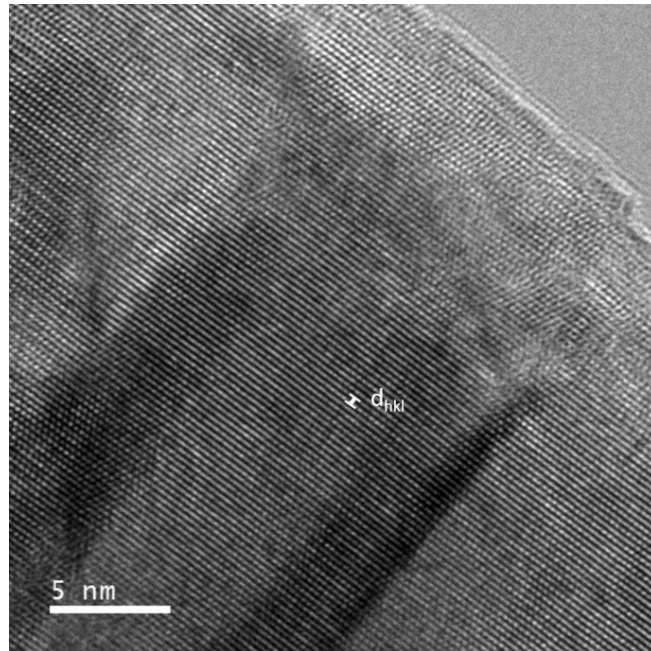


Figure 2. 9 Cross-section high resolution TEM images of GaN close to the $[11\bar{2}0]$ zone axis of GaN thin film.

Contrast in TEM: mass-thickness, diffraction and phase contrast

In TEM imaging, a 3D specimen is represented using a 2D image obtained in transmission, whose contrast is dependent on the interaction between the direct beam and the specimen. The contrast in TEM images can provide useful information about the structure, the composition or the phase of the specimen. Therefore, it is important to fully understand it in order to avoid any misinterpretation. Quantitatively, the contrast in TEM images can be defined as the difference in intensity between two areas of the specimen, according to equation 2.11:

$$C = \frac{I_1 - I_2}{I_1} \quad (2.11)$$

In TEM there are two different types of contrast, namely amplitude and phase contrasts; in addition, amplitude contrast is divided in mass-thickness and diffraction contrasts. Although all of them are always present in some percentage, the microscope is usually set so that one type of contrast largely prevails on the others.

Mass-thickness contrast arises when there are some areas of the specimen with different thickness t or with elemental inhomogeneity. This type of contrast is a direct result of incoherent elastic scattering, such as Rutherford scattering, that is strictly dependent on the atomic number Z and the specimen thickness t . Since the main free path of electrons in the beam is constant, electrons crossing thicker specimens or regions made of heavier atoms are more incoherently scattered off the optic axis. Consequently, due to the small objective aperture, these areas appear darker in the BF images. This type of contrast is particularly important for amorphous, polymeric and biological samples.

Diffraction contrast is fundamental in crystalline specimens and gives information regarding the presence and concentration of defects in the crystal structure. The diffraction contrast arises when the Bragg conditions are satisfied and depends on the coherent elastic scattering of electrons interacting with the specimen. In additions, the diffraction contrast can be enhanced when the two-beam condition is achieved. The two-beam condition can be achieved by tilting the sample, so that only the direct beam and one diffracted beam are strong. Therefore, if there are some defects or misorientations in the specimen for which the Bragg condition is not met, they appear darker in the DF images. Finally, the phase contrast arises from the interference of multiple diffracted beam selected using a larger objective aperture. This contrast is used to obtain HR images and is directly dependent on the specimen thickness t and the excitation error s as shown in the previous section.

In HR images three different types of phase contrasts can be observed: the phase contrast can be visible as lattice fringes, as already described, as Moiré patterns and Fresnel contrast. The Moiré patterns occur when two different crystal structures superimpose, while Fresnel fringes are visible on the edge of out-of-focus objects [129].

Scanning transmission electron microscopy (STEM)

Scanning transmission electron microscopy (STEM) is a TEM mode in which the conventional parallel beam is converged to a focused small probe using condenser lenses C1 and C2 as shown in Figure 2.10.

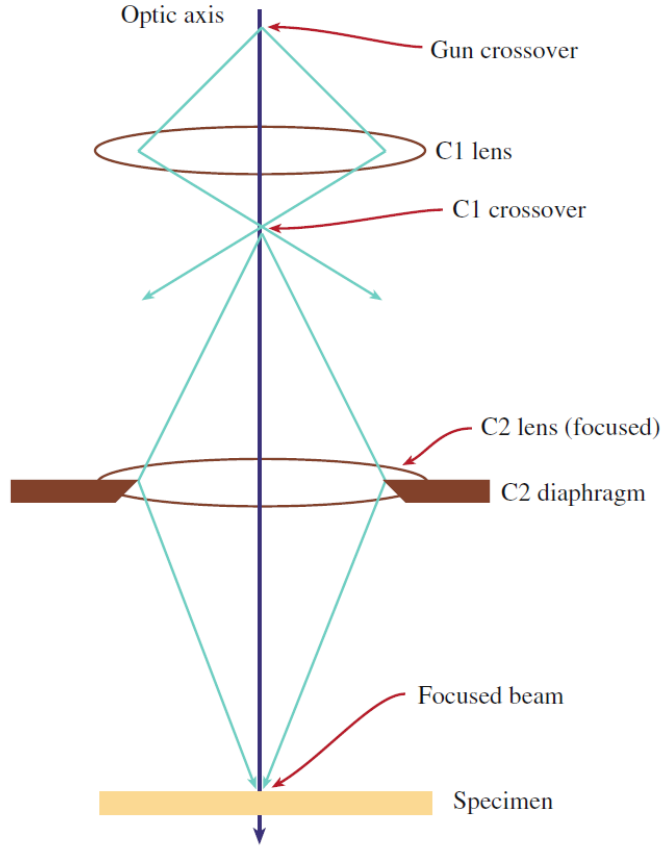


Figure 2. 10 Schematic representation of a TEM used in STEM mode: using a focused C2 lens the electron beam is converged and only a small area of the sample is illuminated. Reprinted by permission from Springer: Springer Nature, “Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 9 The instrument” by D.B. Williams, C.B. Carter, (2009) Copyright <https://link.springer.com/book/10.1007/978-0-387-76501-3> [129].

In STEM mode, the convergent probe is used to raster the specimen, and the scattered electrons are collected at the back-focal plane using a high-angle annular dark-field detector (HAADF). Since the collected electrons are scattered at very high angles, usually about 50 mrad, they do not have a well-defined phase-relationship and Rutherford scattering becomes the main scattering event. Therefore, at these high angles the scattering intensity depends only on the square of the atomic number Z^2 , according to Equation 2.12:

$$\sigma_{Rut} = 1.62 \times 10^{-24} \frac{Z^2}{E_0^2} \cot^2 \frac{\theta}{2} \quad (2.12)$$

Where σ_{Rut} is the scattering cross-section, Z is the atomic number, E_0 is the energy of incident electrons and θ is the deviation angle. Moreover, because of the large area of the detector, a high number of diffraction spots is selected and the interference between them is averaged, causing the suppression of the coherent phase information. Since the contrast of the image is only generated by the incoherently-elastically-scattered electrons, STEM images can be straightforwardly interpreted without using post-

image simulations. In addition, in STEM mode the projection lenses are not used to generate the image, therefore STEM resolution is not limited by lens aberration but only by the size of the convergent probe.

To obtain atomic resolution in STEM mode, it is then necessary that the probe is smaller than the distance between atoms. This is usually obtained by employing highly-bright sources, such as Schottky FEG sources, in which high probe currents and small probe diameters are obtained. However spherical aberration of condenser lenses generally causes a broadening of the probe and a lowering of the microscope resolution. In high-resolution STEMs, this broadening is usually fixed by employing an aberration corrector, which reduces the spherical aberration so that distances as short as 1 Å can be resolved [129].

Energy dispersive X-ray spectroscopy (EDX)

TEM can also be used to obtain elemental information about the specimen using energy dispersive X-ray (EDX) spectra. Since the electrons in the beam are very energetic, when they interact with the electrons of the specimen, excitation of electrons in the inner shell of the specimen atoms may occur. As shown in Figure 2.11, a beam electron excites an inner-shell electron generating a hole in the shell. Electrons from outer levels, then, tend to fill this hole by realising a photon whose energy is equal to the difference between the inner and outer levels in the shell. Since these electrons are in the inner-levels of the atom, the energy of the photon is usually in the range of X-ray and is strictly dependent on the nature of the atoms of the specimen. Such that, by collecting the generated X-ray photons, useful information about the atoms present in the specimen can be obtained. An EDX spectrum is usually collected by adding an EDX detector to the TEM and the intensity and position of the EDX peaks can be used to evaluate the composition and phase of the specimen.

In addition to the nature of the atoms, the position of the EDX peak also depends on the original level of the electron from which it dropped. For instance, if the electrons go from the second inner-level L to the first inner-level K, a K_{α} photon is generated; if the original level of the electron was the third inner level M, then the photon is K_{β} . These additional peaks generated by these secondary photons are often used to study the spectra when the K_{α} peaks overlap. However, their lower intensities might make the quantitative analysis difficult.

EDX can also be used to obtain elemental maps to study the distribution and homogeneity of some elements in the specimen. These maps can be obtained by scanning areas of TEM images taken in STEM mode.

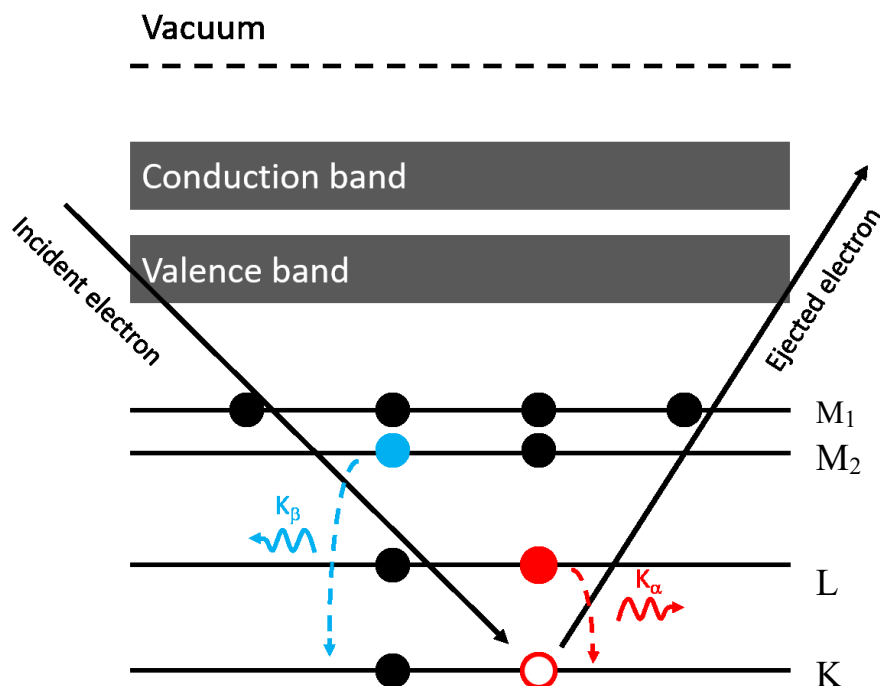


Figure 2. 11 Mechanism of generation of characteristic X-ray photons used to obtain EDX spectra.

In this work, STEM and TEM images and EDX maps were taken using a FEI Philips Tecnai20 with a HAADF detector at 200 kV, while HR-STEM images were obtained using a Titan 80-300 at 300 kV with a probe convergence semi-angle of 15 mrad and spherical aberrations corrector up to the third order. The details about TEM sample preparation are also reported in Appendix B.

2.4 Secondary ion beam mass spectroscopy (SIMS)

Secondary ion beam mass spectroscopy (SIMS) is a high-resolution characterisation technique widely used to analyse composition, impurity levels and depth profile of organic, biological and semiconductor materials. Some of the advantages of these technique are the high surface specificity, high sensitivity and the ability to detect every element in the periodic table, isotopy and molecular species included.

SIMS instruments are usually classified according to the analyser used to detect spattered ions. Time-of-flight (ToF) SIMS is commonly used to characterize the chemical properties of studied materials. A schematic illustration of a TOF-SIMS instrumentation is illustrated in Figure 2.12.

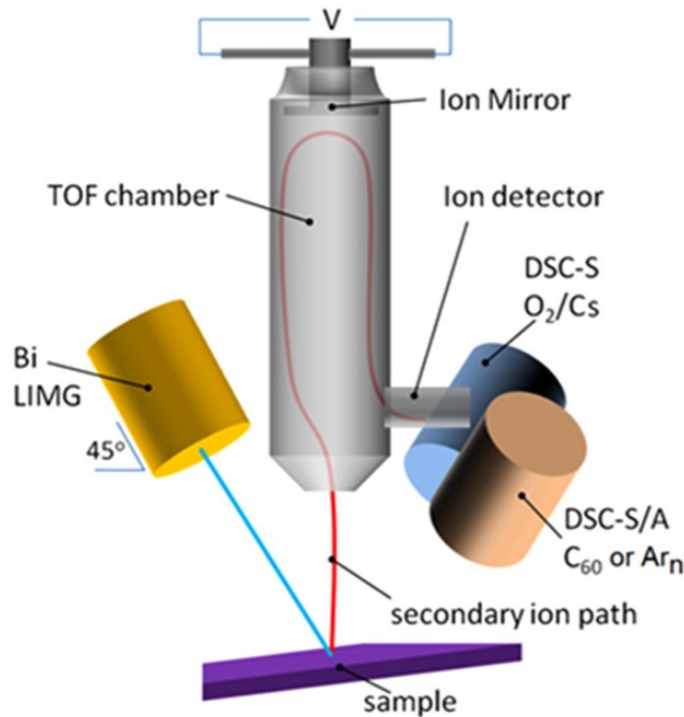


Figure 2. 12 Schematic representation of a ToF-SIMS system. Reused from Fearn et al. [131] with author permission, DOI: <https://doi.org/10.1088/978-1-6817-4088-1>.

In this type of SIMS system, the sample is first introduced in a high-vacuum chamber ($\sim 10^{-8}$ - 10^{-10} mbar), then it is bombarded using a primary ion beam at high energy (0.1-20 keV). Because of this bombardment, several species, such as monoatomic and polyatomic particles, electrons, photons and primary ions are sputtered away from the surface of the sample and collected in a mass spectrometer. The primary ion beam is generally a liquid metal ion gun (LMIG) using small Bi_3^+ clusters as ion source. This Bi_3^+ ion beam is highly focused, so that high lateral resolution is achieved. Once the Bi_3^+ ions interacted with the sample surface, several species with different charge are sputtered and only the desired ones are collected at the analyser separated according to their mass-to-charge ratio (m/z). In TOF-SIMS the collected species are introduced in a time-to-flight analyser where a fixed voltage, usually 2-8 keV, is applied, and then accelerated in a tube of known length L . Once in the analyser, all the species have same kinetic energy and their velocity is strictly dependent on their mass. Therefore, the m/z ratio of each species can be calculated using Equation 2.13 and mass spectra can be obtained [131].

$$\frac{m}{z} = \frac{2Vt^2}{L^2} \quad (2.13)$$

Where V is the applied potential and t is the time necessary to the specie to reach the detector.

In addition to qualitative component analysis, TOF-SIMS can be also used to quantify the concentration of one or more species in the sample. According to the fundamental SIMS equation

(2.14), indeed, the ion current of secondary ions x (I_s^x) is directly proportional to the concentration of that specie x (C_x).

$$I_s^x = I_p C_x S \gamma F \quad (2.14)$$

I_s^x is also dependent on experimental variables, such as the primary ion beam current (I_p), the sputter ion yield (S), the ionisation efficiency (γ) and the transmission of the analysis system (F). Therefore, in order to quantify the concentration of species x , a calibration of the system using standard materials is necessary [131].

Depending on the desired analysis output, TOF-SIMS can be used in three different modes, namely high-resolution mass spectroscopy, chemical ion map and depth profile.

In high-resolution mass spectroscopy, the sample is irradiated by the primary ion beam for a very short time (nanosec), then the sputtered species are collected at the analyser and a mass spectrum is generated. After that, the primary beam can be moved to another spot until the entire predefined area is analysed. In this mode the intensity of the primary ion beam is finely controlled, so that only the most-outcoming layer of atoms are sputtered while the rest of the sample remains preserved. Therefore, if used in this mode, TOF-SIMS is effectively a non-destructive technique. Chemical ion maps can be obtain in the same manner; once the mass spectra is recorded it can be coupled with one specific specie, so that the distribution of the specie can be studied as a function of x,y surface coordinates. Finally, depth profile mode can be used to study the composition of a sample as a function of depth. In this case a second ion beam is necessary, this secondary ion beam is known as sputter ion beam and usually loads Cs^+ or O_2^+ as ion sources. If TOF-SIMS is used in depth profile mode, first the sputter beam rasters the surface of the sample in a predefined area; the high current ($\sim 100\text{mA}$ s) applied to the sputter beam leads to a controlled and constant removal of material during the analysis generating a crater in the sample. Once a layer of material is removed, a smaller area within this crater is irradiated with the primary ion beam and sputtered species are collected at the analyser. The choice of analysing only a small portion of the rostered surface is made to reduce the “edge effect” [131].

It is also worth to stress that when the sputter beam strikes to the sample surface other interactions, in addition to sputter, can happen, such as implantation or chemistry modifications; therefore, it is fundamental to carefully choose the nature of the sputter ions to avoid artefacts and misinterpretations.

In this work SIMS analysis was performed using ION-TOF ToF-SIMS V instrumentations. The primary ion beam was a Bi_3^+ cluster beam accelerated at 25 keV, while the sputter ion beam was using either Cs^+ (1 keV) or O_2^+ (0.5 keV) depending on the purpose of the analysis.

2.5 Optical characterisation

Optical characterisation of thin films is particularly important for those materials that are studied to be employed in optical and optoelectronic applications. For this reason, several techniques, such as UV-visible Transmittance and Reflectance, Photoluminescence and Raman spectroscopies have been used in this work to fully characterize the optical and optoelectronic properties of the materials under study.

2.5.1 Ultraviolet-visible Transmittance and Reflectance spectrophotometry

Ultraviolet-visible (UV-visible) spectrophotometry is a straightforward, non-destructive technique useful to characterize the absorption and reflectance properties of liquids and thin films as well as to evaluate their band gap and refractive index.

Among different techniques that exploit the light-matter interaction to investigate the properties of semiconductor materials, UV-visible spectrophotometry is probably the simplest as well as the most common. A UV-visible spectrophotometer generally consists of a double beam source, which shows a spectral range that spans from near-IR ($\lambda \sim 1200$ nm) to near-UV ($\lambda \sim 200$ nm), a diffraction grating monochromator, to select one wavelength with high resolution, a sample chamber and a detector to measure the transmitted or reflected light. In addition to this standard equipment, several accessories can be added to improve the performance of the instrument or to perform analysis in different modes [132].

When the light reaches the sample, it can be absorbed, transmitted or reflected, depending on the wavelength of the light and the properties of the semiconductor. Therefore, the absorption (A), transmittance (T) and reflectance (R) can be easily obtained using the relation 2.15:

$$A = 1 - T - R \quad (2.15)$$

Transmittance spectrophotometry is the simplest UV-visible analysis and it is based on the relation between the incident light power P_0 and the light power that goes through the sample P_T , as reported in Equation 2.16.

$$T \% = \frac{P_T}{P_0} \times 100 \quad (2.16)$$

To obtain diffuse reflectance spectra, on the other hand, an integrating sphere and dedicated mirrors are required. In this case, the light scattering from the surface of the sample in all directions is measured and compared with the reflectance of a standard sample with known values.

In order to study the optical properties of semiconductor thin films, generally the transmittance, absorption and reflectance are plotted against the wavelength or the energy, calculated according to Equation 2.17 and expressed in eV [133].

$$E = \frac{hc}{\lambda} \quad (2.17)$$

Since the band gap is defined as the forbidden energy levels between the valence and conduction bands, in all these spectra the absorption drops at the energy (or wavelength) of the band gap. Therefore, both the UV-visible transmittance and reflectance spectra can be used to calculate the band gap of the semiconductor thin film, and different formula needs to be used depending on whether the transmittance or reflectance spectra is considered.

If the transmittance spectrum is used, the band gap can be extrapolated from the Tauc plot. In this case first the absorption coefficient is calculated as function of the transmittance T and the thickness t of the thin film (Equation 2.18). Then, the Tauc plot is obtained according to the relation between the absorption coefficient and the band gap E_g , as reported in Equation 2.19. Here n can be $\frac{1}{2}$ or 2 for direct or indirect permitted transitions, respectively. In this Tauc plot, the band gap is equal to the intercept on the x axis of the linear extrapolation of the curve (Figure 2.13a) [134].

$$\alpha = -\frac{\ln(T/100)}{t} \quad (2.18)$$

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2.19)$$

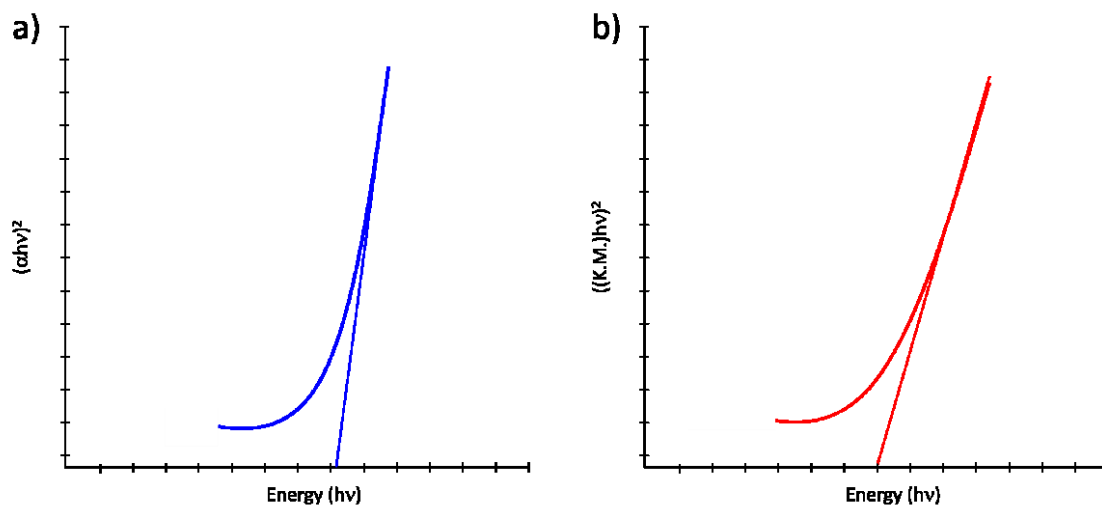


Figure 2. 13 Band gap extrapolation using the Tauc plot (a) and the Kubelka-Munk function (b). The former is obtained from Transmittance data and the thickness of the sample, while the latter is calculated using Reflectance data. In both cases, the band gap is obtained from the linear extrapolation of the curve and is equal to the energy value for y equal to 0.

If, instead, the reflectance spectrum is used, the band gap is obtained by extrapolation of the curve reported in Figure 2.13b. In this case the curve is obtained by calculating the Kubelka-Munk function, which is equal to the ratio between the absorption (k) and scattering (s) coefficients as shown in Equation 2.20. The plot can be obtained by using Equation 2.21 and again the exponent n is equal to $\frac{1}{2}$ or 2 for direct and indirect permitted transitions, respectively.

$$F(R) = \frac{k}{s} = \frac{(1 - R)^2}{2R} \quad (2.20)$$

$$F(R)h\nu = B(h\nu - E_g)^n \quad (2.21)$$

It is then evident that if the Kubelka-Munk function is used, the band gap value is independent on the thickness of the thin film [135], [136].

In this work, all the UV-visible spectra are obtained using an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer. The analysis was carried out at room temperature and with wavelength range spanning from 200 to 800 nm. For the transmittance analysis the baseline was calculated by considering the transmittance of bare sapphire as 100 % transmittance, and by blocking the beam with a black plate as 0 % transmittance.

2.5.2 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a non-destructive, non-contact technique used to investigate the optical and electronic properties of semiconductor thin films.

In general, the luminescence is defined as the spontaneous emission of light by a physical system; photoluminescence is the specific case in which the emission is achieved by the absorption of light from an external source. If a semiconductor material is irradiated by a light with wavelength $h\nu$, electrons in the valence band are promoted in the excited state E_1 in the conduction band, generating electron-hole pairs in the system. Then, the excited electrons return to the ground state E_0 , recombining with holes, through different possible mechanisms, shown in Figure 2.14. According to Stokes' law, if a semiconductor material is irradiated by a light with wavelength $h\nu$, the emitted light must have wavelength equal to or longer than the absorbed light; in the former case (Figure 2.14a) the electron-hole pair recombines using a radiative mechanism, the emitted photon has energy $\Delta E = h\nu$ and the excitation is called resonant excitation. In the latter case (Figure 2.14b), the emitted photon has energy $\Delta E < h\nu$ and part of the excitation energy is dissipated through non-radiative mechanisms, such as thermal vibrations [137], [138].

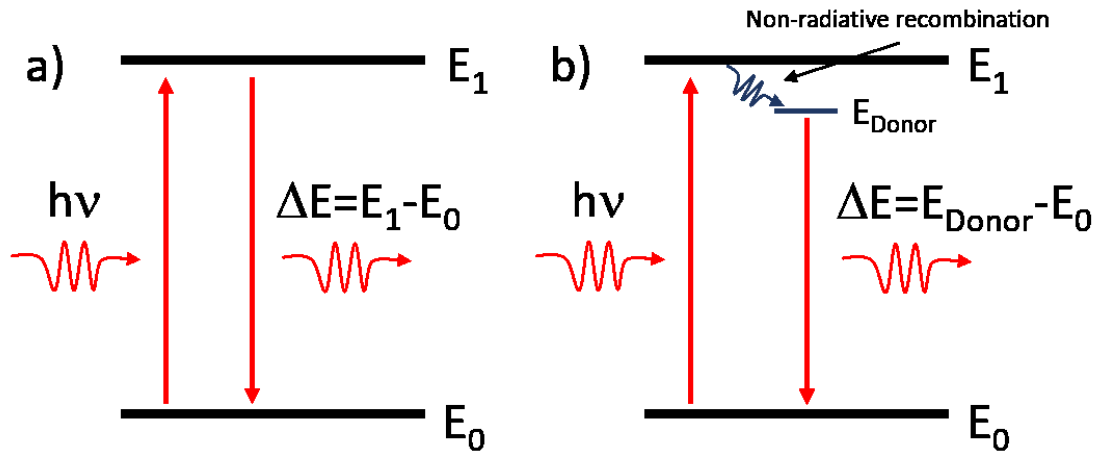


Figure 2. 14 Schematic representation of possible photoluminescence processes.

Since the energy of photons ΔE realised from the recombination of electron-hole pairs is directly related to the band-gap energy between the valence and the conduction band of a semiconductor material, PL spectroscopy can be used to investigate the electronic structure, the band gap and the emission intensity of the material under study. In addition, PL spectroscopy can be a powerful tool to investigate the defect density of semiconductor thin films. Localized defects, such as vacancies, and impurities usually generate localized states within the band gaps, in which excited electrons or holes can be trapped (Figure 2.14b). When the semiconductor thin film is irradiated with light, these trapped electrons and holes can recombine as well, generating luminescence at lower energy than the band gap.

In general, a PL spectrum is obtained by plotting the measured PL emission against the wavelength or $h\nu$ (Figure 2.15). In case of semiconductor thin films, generally two structures are visible in the spectrum: a sharp peak at higher energy and a broad peak at lower energies. The former is related to the radiative recombination of electron-hole pairs and lies at the energy of the band gap; while the latter is related to the presence of defects and impurities, which introduce localized states within the band gap, and gives an estimation of the crystal quality of the thin film.

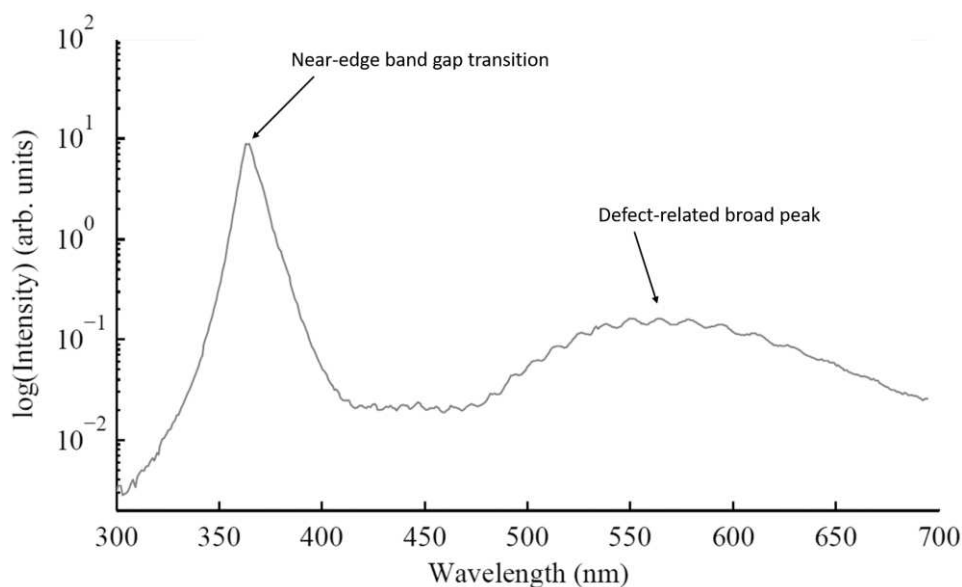


Figure 2. 15 Photoluminescence spectra of GaN at room temperature. The sharp peak is related to the band gap transition, while the broader band gap at larger wavelength is caused by the presence of defects or impurities in the structure.

In addition, low-temperature PL analysis can also be performed to better understand the optoelectronic properties of thin films. If the temperature drops to 77 K (the boiling point of liquid nitrogen), the electron-hole pairs have less thermal energy, therefore unwanted non-radiative processes are frozen, and intensity of PL signals is strongly increased. Low-temperature PL analysis, therefore, can be used to study different energy states that may not be visible at room temperature [138].

In this work PL analysis was performed using an Accent RPM 2000 spectrometer at room temperature. The laser source was operating at wavelength 266 nm and power 1-3 mW, while the diffraction grating was 600 g/mm giving a final wavelength resolution of 0.50 nm. In addition, neutral density filters were inserted to decrease laser power and allow the collection of data at different excitation power.

2.6 Raman spectroscopy

Raman spectroscopy is another non-destructive, non-contact technique used to investigate stress, strain and crystal quality of semiconductor thin films.

When a molecule or a crystal structure interacts with light, this can be either transmitted, absorbed or scattered. While technique such as UV-visible or photoluminescence spectroscopies are based on the first two effects, Raman spectroscopy is based on the scattering of light by the atoms of molecules or crystals. Generally, scattering events can be classified as elastic (or Rayleigh) scattering in which the energy of the incident is equal to the energy of the scattered photon, or inelastic (or Raman) scattering, in which part of the energy of the incident photon is transferred to the atoms. In the latter case, the scattered photon has different energy from the incident photon and this difference is known as Raman shift. Generally, in vibrational spectroscopy this Raman shift is expressed in term of *wave number* $\tilde{\nu}$,

which is directly proportional to the difference of energies between the incident and the scattered photons, as expressed in Equation 2.22.

$$\Delta E = h\nu = hc\tilde{\nu} \quad (2.22)$$

As shown in Figure 2.16, depending on the energy of the incident photon, the electronic transition from the ground state E_0 to an excited state can have magnitude ΔE ranging between 10^{-4} and 10^{10} cm^{-1} ; however, the vibrational interactions, which are relevant for Raman spectroscopy, are usually between 10^2 and 10^4 cm^{-1} .

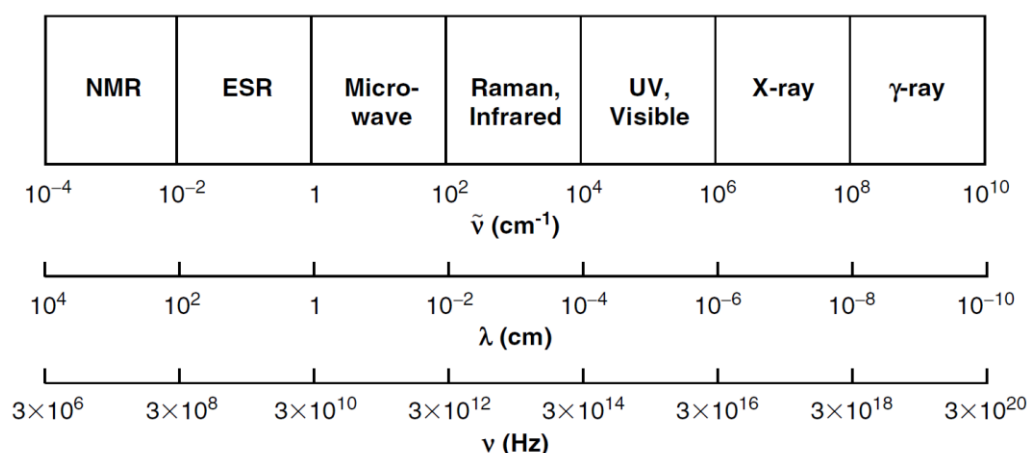


Figure 2. 16 Energy spectrum of electromagnetic wave expressed as wavenumber, wavelength and frequency.. The different spectroscopies used to analyse different portion of the wave are reported in the table. Reprinted from *Introductory Raman Spectroscopy – Chapter 1*, Elsevier book., J. R. Ferraro, Kazuo Nakamoto, Chris W. Brown Copyright (2003), with permission from Elsevier [139], DOI: <https://doi.org/10.1016/B978-0-12-254105-6.X5000-8>.

In a Raman experiment the sample is generally illuminated using a UV-vis laser with frequency ν_0 and the scattered light is detected in the perpendicular direction. In this case, the UV-vis photons interact with the electronic cloud of atoms or molecules and are either elastic or inelastic scattered. Therefore, the detected photons can have same (ν_0), higher ($\nu_0 + \nu_m$) or lower ($\nu_0 - \nu_m$) frequency than the incident photon; where ν_m is the vibrational frequency of the atoms (or molecules). The lines arising from these scatterings are called Rayleigh, Stokes and anti-Stokes line. The Rayleigh lines do not contain any information about the properties of the material, while Stokes and anti-Stokes give the same type of the information; however, the anti-Stokes line are usually few orders of magnitude less intense than the Stokes lines, therefore the Raman spectra usually refer to Stokes scattering. In addition, the Raman spectra is collected in the UV-vis region and the vibrational frequencies ν_m of the materials are obtained as shift from the incident frequency ν_0 [139].

The Raman scattering can be explained using classical physics: if the case of a diatomic molecule is considered, when the molecule interacts with the electromagnetic wave, an electric dipole moment P is induced and can be calculated using Equation 2.23:

$$P = \alpha E = \alpha E_0 \cos(2\pi\nu_0 t) \quad (2.23)$$

Where α is polarizability constant, E_0 is the vibrational amplitude and ν_0 the incident beam frequency. If a molecule vibrates at frequency ν_m , the nuclear displacement q can be defined as

$$q = q_0 \cos(2\pi\nu_m t) \quad (2.24)$$

In addition, if only very small amplitudes of vibration are considered, the polarizability α changes linearly with the displacement q as in Equation 2.25:

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 + \dots \quad (2.25)$$

Where α_0 is the polarizability at the equilibrium position and $(\partial\alpha/\partial q)_0$ is the rate of α variation in function of the displacement q . Therefore, combining the Equations 2.23 – 25 the polarizability can be rewritten as:

$$P = \alpha E_0 \cos(2\pi\nu_0 t) = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial\alpha}{\partial q}\right)_0 q E_0 \cos(2\pi\nu_0 t) \quad (2.26)$$

Which can be rearranged as:

$$\begin{aligned} P &= \alpha E_0 \cos(2\pi\nu_0 t) + \left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 \cos(2\pi\nu_0 t) \cos(2\pi\nu_m t) \\ &= \alpha E_0 \cos(2\pi\nu_0 t) + \frac{1}{2} \left(\frac{\partial\alpha}{\partial q}\right)_0 q_0 E_0 [\cos(2\pi(\nu_0 + \nu_m)t) + \cos(2\pi\nu_0 - \nu_m t)] \end{aligned} \quad (2.27)$$

Where the three terms represent the Rayleigh, the Stokes and the anti-Stokes scattering, respectively. It is then evident that a vibration can be Raman-active if the $(\partial\alpha/\partial q)_0$ term is non-zero, therefore to see a peak in the Raman spectra, it is necessary that the polarizability value is altered during the vibration.

However, both the electric field E and the electric dipole mode P are vector with component in the three directions x , y and z , therefore Equation 2.23 has to be rewritten as:

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} a_{xx} & a_{xy} & a_{xz} \\ a_{yx} & a_{yy} & a_{yz} \\ a_{zx} & a_{xy} & a_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} \quad (2.28)$$

Here, the second matrix is called the polarizability tensor and is symmetric in normal Raman. Therefore, according to Equation 2.27 a vibration is Raman-active if one of the component of the polarizability tensor varies during the vibration [139].

While the above theory is viable for a system of single molecules, in the case of crystals the observed vibrations are the result of collective oscillations occurring in the entire lattice of the crystal. Since these oscillations are quantized, they are usually called *phonons*. Although, a crystal could show very complex vibrations, all of them can be classified as linear combination of four fundamental modes.

These fundamental modes are characterized as a function of direction, which are longitudinal (L) and transversal (T), and frequency, optical (O) and acoustic (A), giving the four modes LO, LA, TO and TA. In addition, in order for a vibration to be propagate throughout the crystal structure, it is necessary that the atoms in the structure vibrate in phase; therefore, the lattice vibrations visible in Raman spectra are strictly related to the symmetry of the crystal structure under study. Generally, the vibrations in a crystal can be classified in 4 different classes, namely A, B, E and T; where A and B represent degenerate vibrations along the *c*-axis, E refers to doubly degenerate vibrations normal to the *c*-axis and T represents triply degenerate vibrations. In Figure 2.17 the phonon modes visible in wurtzite GaN structure are reported [140].

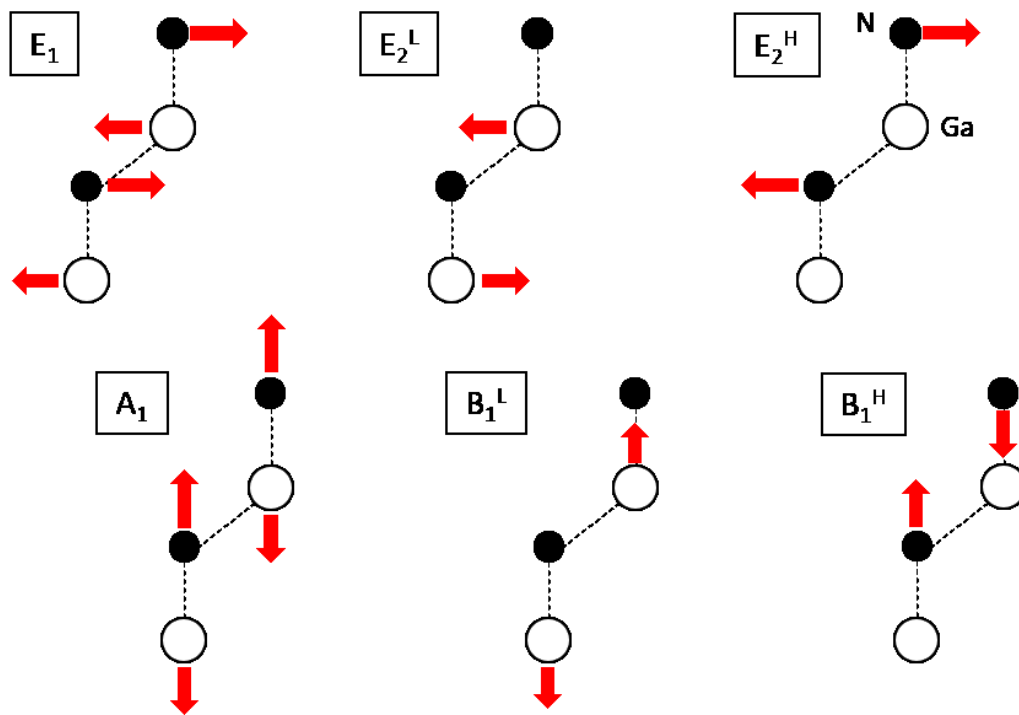


Figure 2. 17 Possible phonon modes present in a GaN wurtzite structure. Reprinted from Hiroshi Harima 2002 *J. Phys.: Condens. Matter*, 14, R967, © IOP Publishing. All rights reserved [141], DOI: <https://doi.org/10.1088/0953-8984/14/38/201>.

In this work an InVia Raman spectrometer is used to measure the Raman spectra of the thin films under study. In this spectrometer the sample is loaded in a closed chamber, then an optical microscope can be used to choose the area to illuminate. Then the surface of the sample is illuminated using a UV-visible laser with wavelength of 532 nm and spot size of 1 μm . After interaction with the sample, the scattered photons pass through the diffraction grating (1800 g/mm) and finally reach the detector. In Figure 2.18 a schematic representation of a Raman spectrometer is reported. The resolution of the Raman spectra depends on the laser wavelength, the focal length, which is the distance between the grating and the detector, and the density of the diffraction grating.

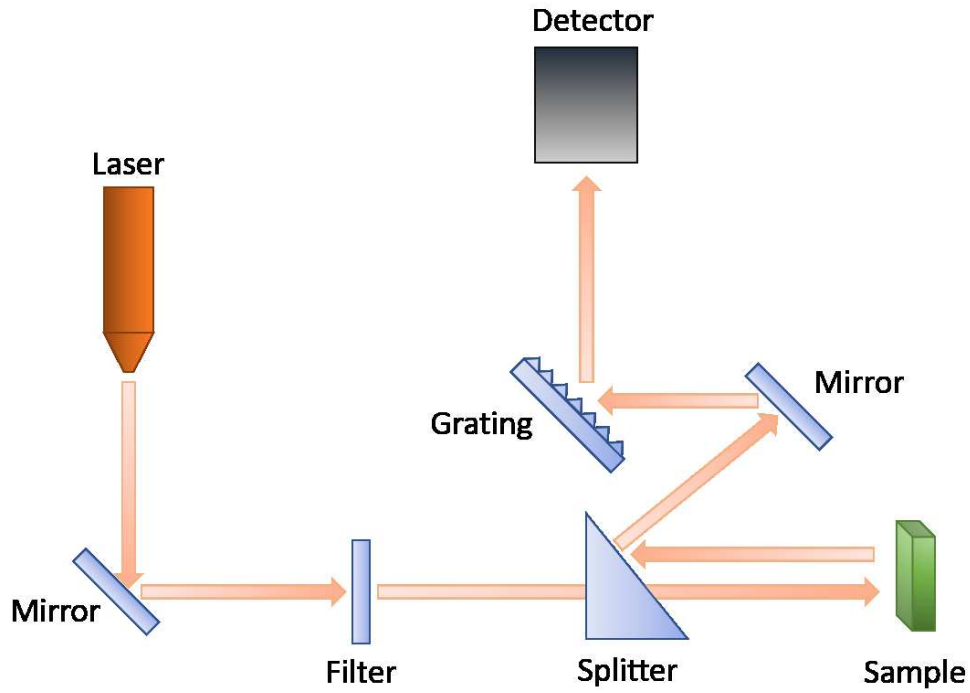


Figure 2. 18 Schematic representation of the Raman spectrometer structure.

2.7 Electrical characterisation

Electronic devices based on semiconductor materials have now achieved outstanding performances in terms of efficiencies, reliability and lifetime. However, due to the constant need to further improve these performances, new materials need to be proposed in order to meet the high-demanding requirements. For these reasons, the electronic properties of the materials investigated in this work are characterized using Hall effect measurement technique.

2.7.1 Hall effect measurements

In 1879 Dr Edwin Hall discovered the phenomenon [142] that now bears his name. While he was studying the effect of electrical current applied to a thin rectangle of gold placed in a magnetic field, he noted that when a magnetic field is applied a small net voltage is measured perpendicular to the magnetic field.

An example of this effect is shown in Figure 2.19: a very thin, *p*-type semiconductor material, in which the electrons are constrained to move only along the *x* and *y* directions, is introduced in a magnetic field *B* oriented along the *z* direction [143]. If a constant current *I* flows in the semiconductor along the *x* direction, a Lorentz force *F_L* arises according to Equation 2.29

$$\mathbf{F}_L = q(\mathbf{v} \times \mathbf{B}) = -qv_x B_z \quad (2.29)$$

Where v_x is the velocity of carrier in x direction, and for p -type semiconductors it is defined as in Equation 2.30

$$v_x = \frac{I}{qtWp} \quad (2.30)$$

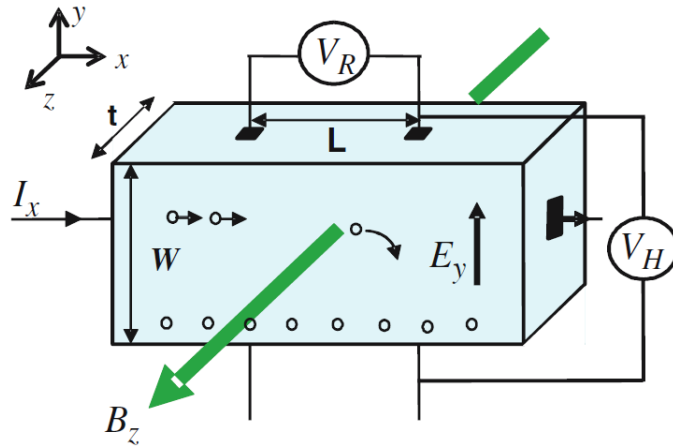


Figure 2. 19 Schematic representation of the Hall effect in a p -type semiconductor. Reprinted by permission from Springer: Springer Nature, “Electrical characterization of semiconductor materials and devices—review” – Deen, M.J. & Pascal, F. *J Mater Sci: Mater Electron* (2006) 17: 549, (2006) Copyright. [143], DOI: <https://doi.org/10.1007/s10854-006-0001-8>.

Due to the presence of this Lorentz force, an excess of surface electrical charges arises on one side of the sample, generating an electric field E_y along the y direction, perpendicular to both the applied magnetic field and the flowing current. (Figure 2.19). In addition, when the steady state is achieved, the two active forces in the system, namely the Lorentz force F_L and the electric force F_{EL} , balance, and the Hall voltage V_H can be calculated (Equations 2.31 and 2.32).

$$F = F_L + F_{EL} = -qv_x B_z + qE_y = 0 \quad (2.31)$$

$$E_y = \frac{BI}{qtWp} \text{ and } V_H = E_y W = \frac{BI}{qtp} \quad (2.32)$$

Where t and W are the thickness and the width of the sample, respectively.

Therefore, by measuring the Hall effect of a thin film, fundamental electrical parameters, such as sheet carrier density, sheet carrier mobility and resistivity can be directly determined. Since both the magnetic field B_z and the flowing current I are known, the sheet carrier concentration can be calculated as function of the Hall voltage V_H (Equation 2.33) [143].

$$p_s = \frac{BI}{qV_H} \quad (2.33)$$

In addition, if the thickness of the thin film t is known, both the Hall coefficient R_H (Equation 2.34) and the bulk carrier density p (Equation 2.35) can be calculated.

$$R_H = \frac{tV_H}{BI} \quad (2.34)$$

$$p = \frac{1}{qR_H} \quad (2.35)$$

Similar calculations can be performed for n -type semiconductors; however, it must be noticed that in this case both the Hall coefficient R_H and the bulk carrier concentration n have negative signs.

Finally, if the resistivity ρ is known, the carrier mobility can be calculated as shown in Equation 2.36.

$$\mu = \frac{|R_H|}{\rho} \quad (2.36)$$

Since all the critical electrical parameters can be evaluated in only one measurement, Hall measurements has now become the most widely used technique to evaluate the electronic properties of semiconductor materials [143].

The Hall effect is generally measured using two different geometries. The first one is the Hall bar geometry, in which the sample is shaped in a long bar and at least six different contacts must be applied; different geometries of possible Hall bars are shown in Figure 2.20.

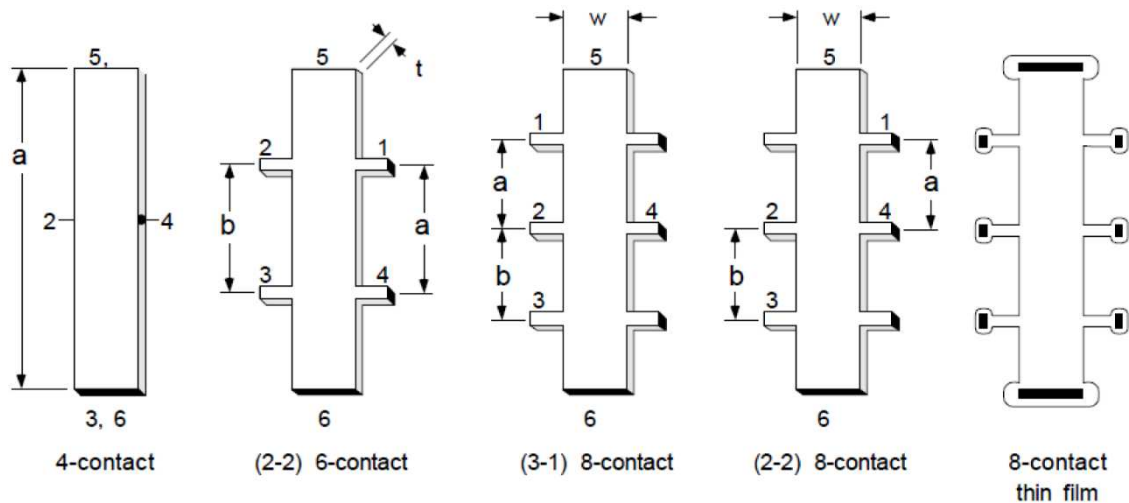


Figure 2. 20 Schematic representation of Hall bar geometries for Hall measurement [144].

In presence of a magnetic field B , the Hall voltage V_H is measured by applying the current flowing from contact 5 to contact 6 and measuring the voltage across contacts 1 and 2 or 3 and 4. Then the bulk

resistivity of the sample can be calculated using Equation 2.37, where the voltage drop between contacts 1 and 3 is calculated in absence of any magnetic field.

$$\rho = \frac{V_{1,3}wt}{I_{5,6}b} \quad (2.37)$$

Where w and t are the width and thickness of the sample, while b is the distance between contacts 1 and 3 [143].

Although Hall bar geometries are still commonly used to measure the Hall effect, there are some disadvantages such as the need of at least six contacts to perform the measurement and the requirement to measure the exact distance between contacts, which could be challenging.

Therefore, a second geometry, called Van der Pauw geometry, is now becoming much more popular for performing Hall measurements. As shown in Figure 2.21, in this geometry only four contacts are necessary, as long as they are sufficiently small, near the edge of the sample and the thickness of the sample is sufficiently uniform. In theory any shape of the sample could be used to perform the analysis, however a symmetrical shape is usually preferred.

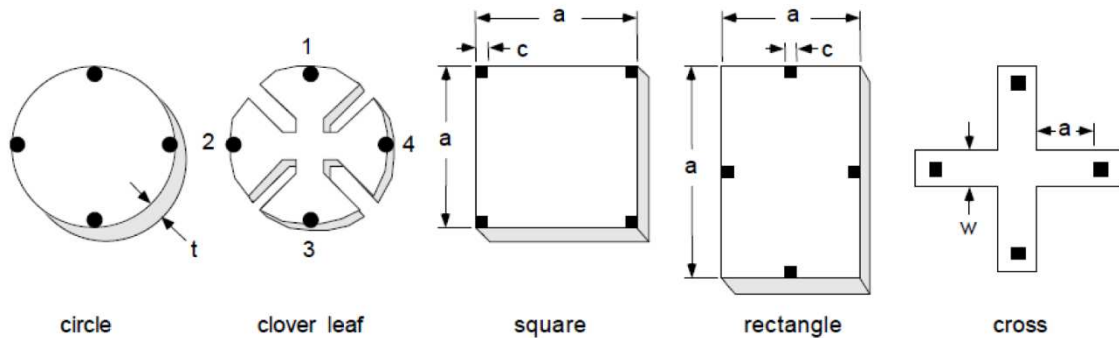


Figure 2. 21 Different Van der Pauw geometries for Hall measurement [144].

In this case the current is flowing across two adjacent contact ($I_{1,2}$) and the potential drop is measured between the two other contact ($V_{3,4}$), in presence of a magnetic field B . In addition, the resistivity is calculated by measuring resistances R_A and R_B in absence of magnetic field, as shown in Equations 2.38, 39 and 40.

$$\rho = \frac{\pi t}{\ln 2} \times \frac{(R_A + R_B)}{2} \times f \quad (2.38)$$

$$R_A = \frac{V_3 - V_4}{I_{1,2}} \quad (2.39)$$

$$R_B = \frac{V_4 - V_1}{I_{2,3}} \quad (2.40)$$

Where f is the correction factor. Finally, concentrations and mobility of the carriers can be calculated using the same formulas used for Hall bar geometry [143].

Compared to Hall bar geometry, Van der Pauw method is easier to use, as only four contacts are necessary; however, the measurements usually take longer time and are highly sensitive to the contact size and the contact distances.

In this work, Hall measurements were performed using Van der Pauw geometry, as shown in Figure 2.21a. Four indium contacts are applied on the sample, using a high temperature pen heated at 160°. Then the sample is loaded on a solder pad sample card and connected to the circuit using four copper wires. The solder card is then loaded in a Model 8404 AC/DC Hall Effect Measurement System to perform the measurement at room temperature.

First the ohmic nature of the indium contacts was checked by applying 20 μA of current. Then both the resistivity and the Hall voltage were measured in absence and presence of a magnetic field of 1.6 T. The final results were then elaborated using *Lake Shore* software.

Chapter 3

Characterisation of GaN

3.1 Introduction

GaN has become very popular over the last few decades for both optoelectronic and electrical devices due to its wide, direct band gap (3.4 eV), high saturation velocity ($2.25 \cdot 10^7$ cm/s [3]) and high electron mobility (900 cm²/Vs [3]). However, the performance of these devices largely depends on the crystal quality of GaN thin films and great effort has been made to reduce the density of defects present in the GaN structure [14], [48], [96]. In this chapter GaN thin films grown using e-beam physical vapour deposition (e-beam PVD) are studied. Since e-beam PVD is not commonly used to grow binary III-nitride materials, the properties of binary GaN grown using this technique were first investigated before moving to more complex systems such as ternary ScGaN or FeGaN. In addition, the performance of devices based on stack of different epilayers, such as LEDs or HEMTs, generally improves when the epilayers are grown consecutively without taking the thin films out of the system and exposing GaN to air. Therefore, it is of technological interest not only studying the properties of ternary transition metal nitrides but also of binary GaN on which these materials will be grown in the final device. For this reason, in this chapter the properties of GaN thin films grown using e-beam PVD in different growth conditions are first investigated, before moving on transition metal-based GaN thin films.

3.2 Growth rate

In devices such as HEMTs and LEDs the thickness of each layer influences the properties of the entire device; therefore, it is crucial to achieve fine control of the thickness of the thin film and of the growth rate at which it is grown. The growth rate is usually expressed in nm/h and it is obtained by measuring the thickness of the thin film using *ex situ* techniques such as TEM or SEM. This parameter is strictly dependent on the chosen growth conditions such as the temperature at which the substrate is heated (T_{sub}) or the ratio between reactants in the chamber (III/V ratio). Generally, when GaN is grown, the substrate temperature is chosen to be between 600 and 800 °C [104]: for lower temperatures the mobility of the adatoms is too low, leading to highly-defective thin films, while for higher temperatures the desorption and decomposition of precursors become very fast, leading to low growth rates and rough surfaces, as shown in Chapter 4. For this reason, the GaN thin films studied in this chapter have been grown using a substrate temperature equal to 800 °C.

The III/V ratio is also a crucial parameter that influences both the growth rate and the properties of the final thin film. Depending on the value of this ratio the growth can take place either in Ga- or in N-rich conditions. When Ga-rich conditions are chosen, the growth rate is limited by the concentration of nitrogen near the surface of the substrate, where the deposition takes place. Because of that, in these conditions the growth rate is independent of the Ga evaporation rate and, in turn, on the Ga e-beam current used. In addition, since the availability of nitrogen is limited, when Ga adatoms reaches the surface they tend to diffuse before reacting with nitrogen, leading to very smooth surfaces [145]. On the other hand, when the growth occurs in N-rich conditions, the growth rate is limited by the concentration of Ga near the surface of the substrate. As a result, small variations of Ga evaporation rates result in large variations of GaN growth rates. Moreover, because of the high concentration of nitrogen, when Ga adatoms reach the surface of the substrate they quickly react before diffusing on the surface. Such that, when the growth takes place in N-rich conditions rougher surfaces made of rounded nanocrystallites are usually obtained [105].

With the aim of studying the influence of Ga evaporation rate on the growth rate of GaN when e-beam PVD is used, GaN thin films were grown on sapphire using different Ga e-beam currents while all the other variables remained unchanged. The growth rates of GaN grown using Ga e-beam currents ranging between 73 and 85 mA are illustrated in Figure 3.1. TEM cross-section imaging was used to measure the thin film thicknesses, which are listed in Table 3.1. When the lowest Ga e-beam current was used (Sample A), the growth rate is as low as 10.6 nm/h, and after 90 minutes of growth the thin film is 16 nm thick. Such a low growth rate suggests that when the Ga e-beam current is only 73 mA, the evaporation of Ga is very slow and the concentration of Ga near the surface of the substrate is not high enough to efficiently react with nitrogen and deposit GaN. However, when the Ga e-beam current is increased of few milliamperes, the growth rate increases of about 1 order of magnitude from 10.6 nm/h for 73 mA to 106.7 nm/h for 76 mA (Sample B). This large increase of growth rate suggests that 76 mA

is the minimum current intensity necessary to trigger the evaporation of Ga, so that the concentration of Ga near the substrate surface is high enough to deposit good-quality GaN thin film. When the e-beam current is further increased from 76 mA to 79 mA (Sample C) and 82 mA (Sample D) the growth rate increases up to 122.7 nm/h and 120 nm/h, respectively. In Figure 3.1 the dependence of the growth rate on the Ga e-beam current can be observed clearly, suggesting that these thin films are grown in N-rich growth conditions. However, no references regarding GaN-growth properties using e-beam PVD are currently available and *ex-situ* characterisation techniques, such as AFM, are necessary to confirm the N-rich growth regime.

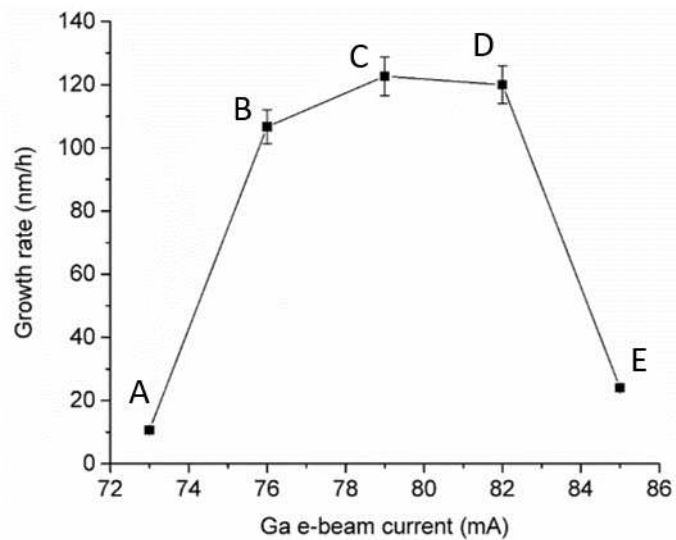


Figure 3. 1 Growth rate plot of GaN grown using different Ga e-beam currents. The dependence of the growth rate on the e-beam current used suggests that the growth takes place in N-rich conditions.

Name	Ga e-beam current (mA)	Thickness (nm)	Growth rate (nm/h)
A	73	16	10.6
B	76	160	106.7
C	79	184	122.7
D	82	180	120
E	85	36	24

Table 3. 1 Ga e-beam currents, thicknesses and growth rate of all GaN samples under study. The thickness was calculated using cross-section TEM imaging.

It is also interesting to notice that when the e-beam current is further increased from 82 to 85 mA (Sample E), the growth rate suddenly drops down to 24 nm/h. A possible explanation for this drop could be that for this e-beam current the evaporation of Ga becomes very fast, so that high concentration of Ga adatoms accumulate on the surface of the substrate lowering the rate of GaN deposition. A similar growth rate trend was reported when GaN was grown using MBE and MEE (migration-enhanced epitaxy). Kawaharazuka and collaborators [146] observed that when the flux of Ga exceeded a certain limit value the growth rate dropped; they related this drop to the accumulation of Ga monolayers and Ga droplets on the surface of deposited GaN. Since the diffusion of nitrogen in metallic Ga is slow, the

presence of these accumulations lowers the overall growth rate of the deposition of GaN [146]. However, if such a high III/V ratio is present during the growth of Sample E, the surface of the sample would be expected to show typical Ga-rich or Ga-droplet morphology [145]. However, as shown in Section 3.2, GaN grown using the highest e-beam current does not show a smooth surface as expected. Furthermore, the growth rate of this thin film is comparable to that of GaN grown using an e-beam current equal to 73 mA (Sample A). This similarity might suggest that the lower growth rate of GaN grown using the highest e-beam current might be due to some experimental failure of the system that was not detected during the experiment.

3.3 Surface morphology

The studies of morphological properties of semiconductor thin films is of interest for many applications, such as optoelectronics or device processing. In addition, surface characterisation techniques can be used to investigate the mechanism and growth conditions of these thin films. In this work the surface properties of GaN grown using different Ga e-beam currents are investigated using AFM and plan-view TEM imaging.

The $1 \times 1 \mu\text{m}^2$ AFM images of the GaN thin films under study are shown in Figure 3.2. All GaN thin films show surfaces made of rounded 3D nanocrystallites of different sizes. This morphology suggests that the growth of GaN thin films takes place in N-rich conditions for all samples. In N-rich conditions, the growth is limited by the availability of Ga adatoms near the surface of the substrate, and when Ga adatoms reach the substrate they react with nitrogen before diffusing. The fast reaction with nitrogen results in a 3D growth mechanism and surfaces made of 3D nanocrystallites [105], [145]. Tarsa and collaborators [105] have proposed a qualitative model to explain the surface properties of GaN grown in N-rich conditions. They suggested that in sufficiently N-rich conditions the outmost layer of GaN is expected to be made of N atoms that are bonded only with one Ga atom of the layer beneath them, while the other remaining three bonds are “dangling”. Therefore, when a Ga atom reaches the N-rich surface it easily forms a Ga – N bond, and an energy barrier must be overcome in order for the Ga atom to break this bond and diffuse to another site [105].

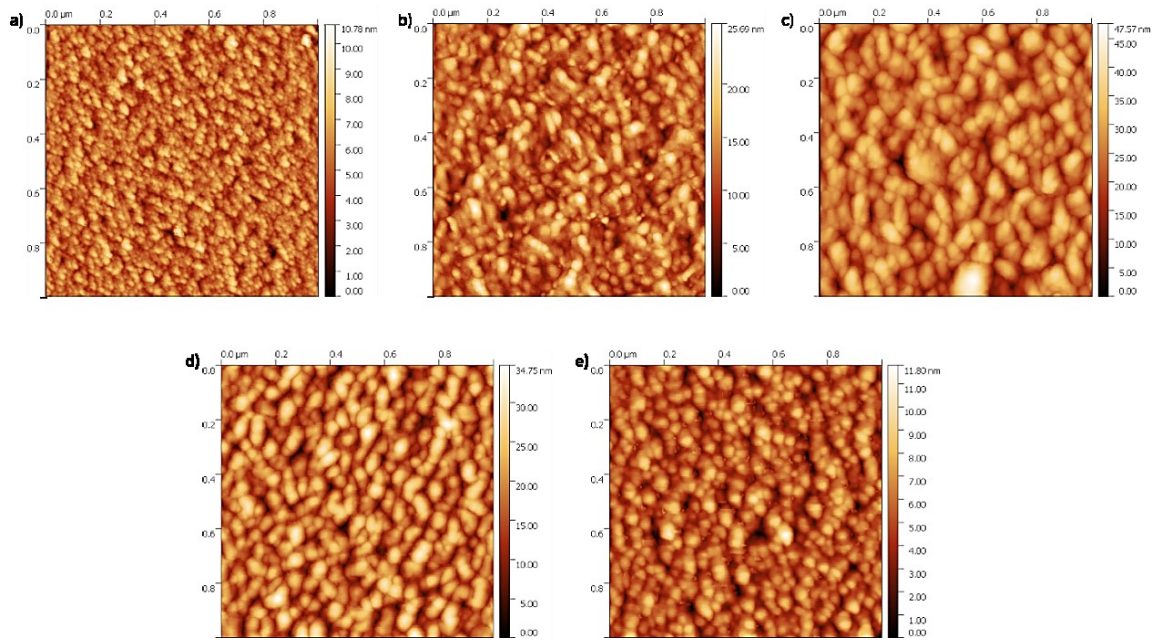


Figure 3. 2 $\times$ 1 μ m AFM images of GaN grown using Ga e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e). All AFM the images are processed using parabolic flattening.

These AFM results are in agreement with the growth rates discussed in the previous section, which suggested that the growths take place in N-rich regime. According to the growth rate results, however, a different surface morphology was expected when the e-beam current was further increased to 85 mA (Sample E). As discussed in the previous section, when the e-beam current is increased from 82 to 85 mA, the growth rate drops, suggesting that high concentration of unreacted Ga might limit the deposition rate of GaN. However, the surface morphology of this sample remains comparable to the ones of the rest of the set, suggesting that even at this e-beam current the growth still takes place in N-rich conditions. These contradictory results for Sample E are yet unclear and further investigation appears to be necessary to understand the real conditions in which this growth was carried out.

In Figure 3.3a the size of nanocrystallites of GaN thin films grown using increasing e-beam currents are shown. A clear relationship between nanocrystallite size and Ga e-beam current can be observed: when the e-beam current increases from 73 mA to 82 mA the nanocrystallite size increases from 16 nm to 61 nm. This increase of size can be related to an improvement of crystal quality of GaN thin films, as confirmed by XRD and TEM results shown in the following section. When the Ga e-beam current is further increased from 82 to 85 mA, the nanocrystallites become smaller and comparable to the thin film obtained using e-beam current equal to 76 mA. This drop in crystal size suggests that when the e-beam current exceeds 82 mA the crystal quality of the thin film decreases. It is possible that this decrease in crystal quality is related to the excessively fast evaporation of Ga at this e-beam current; however, a failure of the system that was not detected by the software is also a possibility. Nonetheless, the results shown in Figure 3.3a suggest that for the growth of GaN using e-beam PVD in these conditions, the

optimal range of Ga e-beam current lies about 82 mA. This result is in good agreement with XRD and TEM results discussed in this chapter.

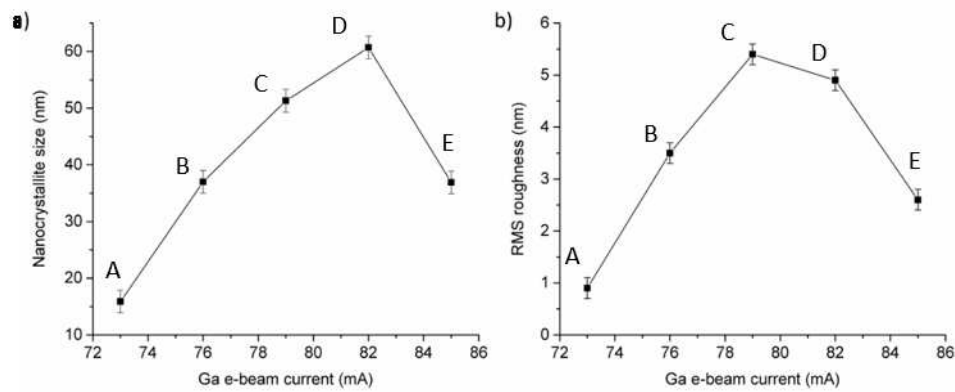


Figure 3. 3 Nanocrystallite size (a) and root-mean-square roughness (b) of GaN grown using increasing Ga e-beam current measured from AFM images illustrate in Figure 3.2.

The root-mean-square (RMS) roughness values of these thin films are plotted in Figure 3.3b. All thin films show a relatively smooth surface, with RMS values ranging between 0.9 and 5.3 nm. These low RMS values suggest that smooth GaN with relatively good surface quality can be obtained by using e-beam PVD in these growth conditions.

Finally, plan-view TEM imaging was used to investigate further the properties of GaN surfaces. In Figure 3.4 a and b bright-field (BF) and dark-field (DF) TEM images of GaN grown using 82 mA as e-beam current are illustrated. As expected from AFM results, rounded nanocrystallites are clearly visible in BF images, suggesting that in these conditions GaN thin films grow via an island growth mechanism rather than a layer growth one [147]. Moreover, in both TEM images misoriented nanocrystallites are also visible: these results are in good agreement with the island growth mechanism and are confirmed by the width of the rocking curves shown in the following section. Similar plan-view TEM results were also observed for the other GaN thin films studied in this chapter (not shown).

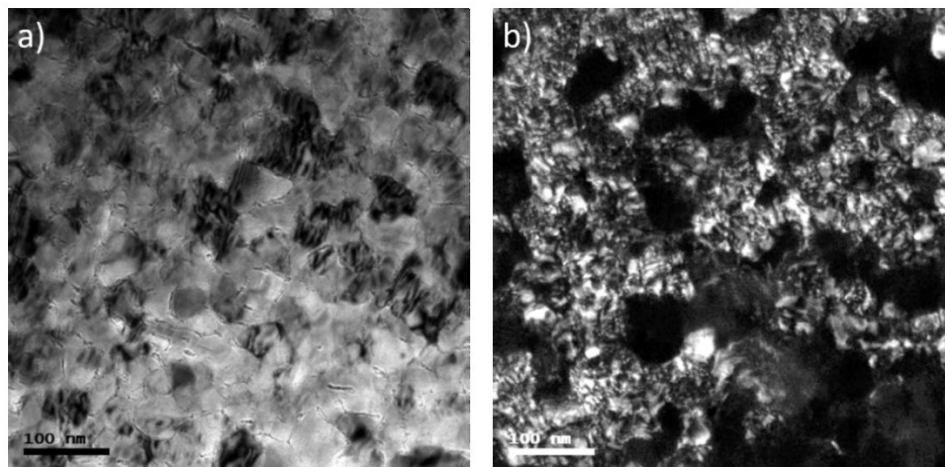


Figure 3. 4 Bright-field (BF) (a) and centred-dark-field (CDF) (b) plan-view TEM images of GaN grown using Ga e-beam current equal to 82 mA.

3.4 Structural and microstructural characterisation

The properties of the crystal structure of GaN thin films grown using different Ga e-beam currents are discussed in this section. HR-XRD in $2\theta-\omega$ geometry was used to confirm the epitaxial growth of the thin films, evaluate the crystal structure and calculate the c lattice parameter. The XRD patterns of the thin films are illustrated in Figure 3.5a-e. In all patterns only the peaks at 34.6° and 72.9° can be related to GaN, and specifically to the (002) and (004) planes of hexagonal GaN. The absence of other peaks attributable to GaN confirms that all GaN thin films have been successfully grown along the preferential [0001] direction on the top of sapphire substrates. Moreover, the (002) and (004) peaks of GaN structure indicate that these GaN thin films are stable in the wurtzite structure without extended cubic inclusions. The calculated c lattice parameters are listed in Table 3.2. The a parameter, on the other hand, could not be calculated using HR-XRD since it was not possible to carry out the experiment using asymmetric geometries. As shown in Table 3.2, the c lattice parameters of the GaN thin films under study are all larger than the theoretical value reported in literature at 300°C ($5.1851 \text{ \AA}$ [148]). The larger lattice parameter suggests that all the thin films are under different degrees of tensile strain (Table 3.2). This strain might arise from the need to accommodate the lattice mismatch with the underlying sapphire substrate. The strain present in these thin films was also studied using c/a ratios calculated from diffraction patterns and will be further discussed later in this section.

Sample	Ga e-beam current (mA)	(002) peak position ($^\circ$)	c lattice parameter ($\text{\AA}$)	Strain $\left(\frac{c_{\text{exp}} - c_{\text{ideal}}}{c_{\text{ideal}}}\right)$
A	73	34.53966	5.1894 ± 0.0006	+ 0.000829
B	76	34.54902	5.1882 ± 0.0003	+ 0.000598
C	79	34.54349	5.1889 ± 0.0005	+ 0.000733
D	82	34.535	5.1901 ± 0.0007	+ 0.000964
E	85	34.5495	5.18704 ± 0.00004	+ 0.000374

Table 3. 2 Position of (002) peaks measured from $2\theta-\omega$ scans of GaN grown using increasing Ga e-beam current. The calculated c parameters and strain in the thin films are also reported.

It is also interesting to notice that the intensity of the (002) peaks shown in Figure 3.5 largely changes when the Ga e-beam current changes. One possibility is that this variation in intensity might be related to a variation of crystal quality of the thin film structure. However, since both sample A and E are much thinner than the rest of the samples, it is also possible that the less intense peaks are merely due to a difference in thicknesses.

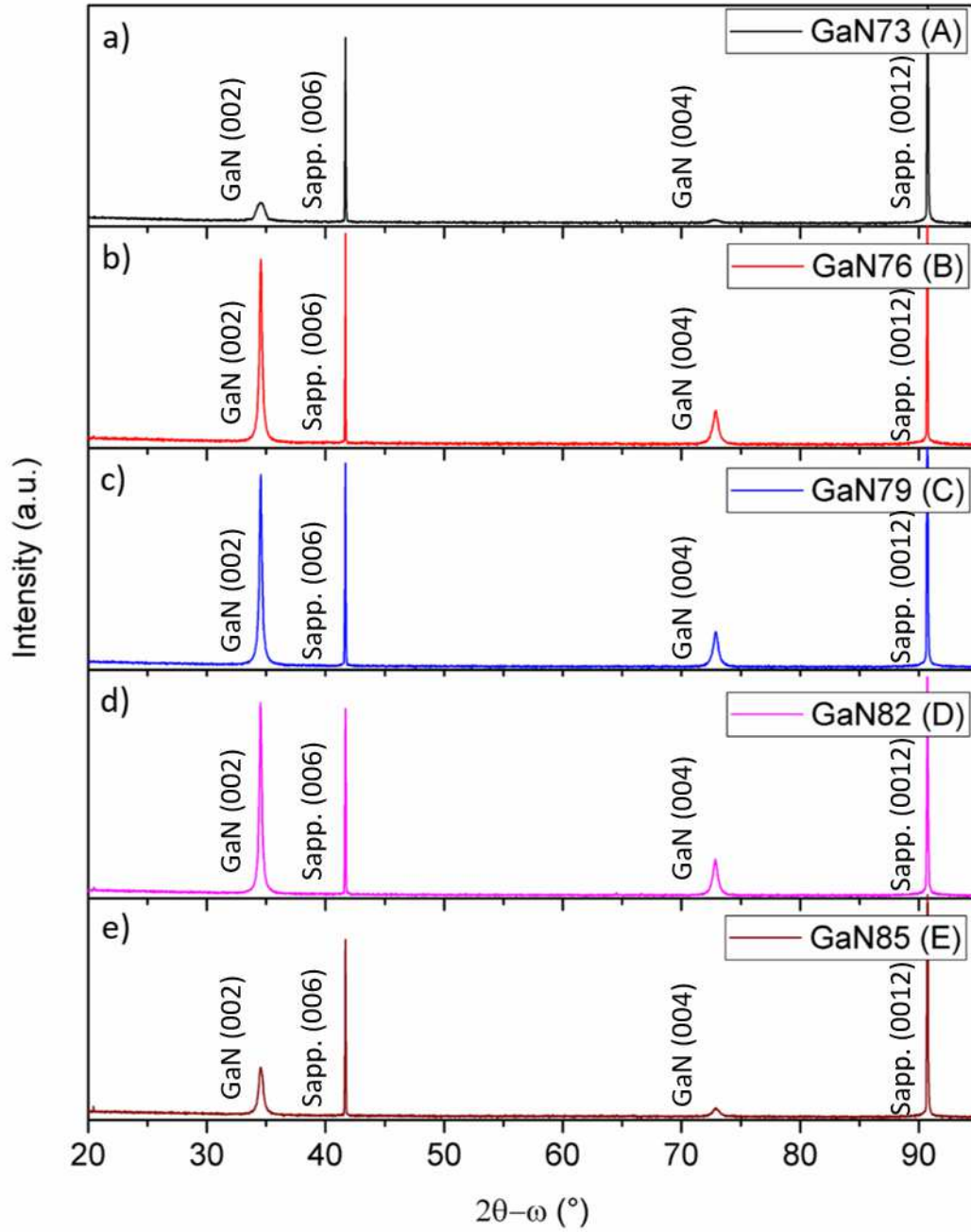


Figure 3. 5 2θ - ω scans of GaN grown using e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e).

Therefore, to more accurately study the crystal quality of GaN thin films grown using different e-beam currents, HR-XRD ω scans (rocking curve) were obtained. The rocking curves obtained are shown in Figure 3.6 and the full-width-half-maximum (FWHM) values reported in Table 3.3. Although the XRD results obtained using ω scan are generally considered mostly independent from thickness offsets, it is worth noticing that even in this case the thinner samples (A and E) show less intense peaks. However, the FWHM values obtained from these rocking curves (Table 3.3) are in perfect agreement with the AFM nanocrystallite sizes reported in Section 3.3. While the GaN obtained using the lowest

(73 mA) and highest (85 mA) e-beam current give rise to larger peaks with width close to 2° , the thin films grown using intermediate e-beam currents show an improved crystal quality, as expected from AFM results.

Therefore, these rocking curve results confirm that the optimal Ga e-beam current GaN grown using e-beam PVD in these conditions lies in the range between 79 and 82 mA. If higher currents are used the crystal quality quickly drops, possibly due to the excessively fast evaporation of Ga; if lower currents are used the crystal quality decreases as well, although the reduction is much slower. Although from these results 82 mA appears to be the optimal e-beam current, further optimization of the growth conditions is still necessary. All rocking curves reported in Figure 3.6, in fact, have FWHM higher than 1° , suggesting that misorientations are present in all thin films, even in the optimum one (Sample D). The presence of misorientations was also confirmed by the plan-view TEM images illustrated in the previous section and are typical of 3D island nucleation mechanism. Therefore, the optimization of other growth parameters, such as substrate temperature (T_{sub}) or nitrogen pressure (p_{N_2}) could be useful to improve the crystal quality of GaN thin film grown using e-beam PVD.

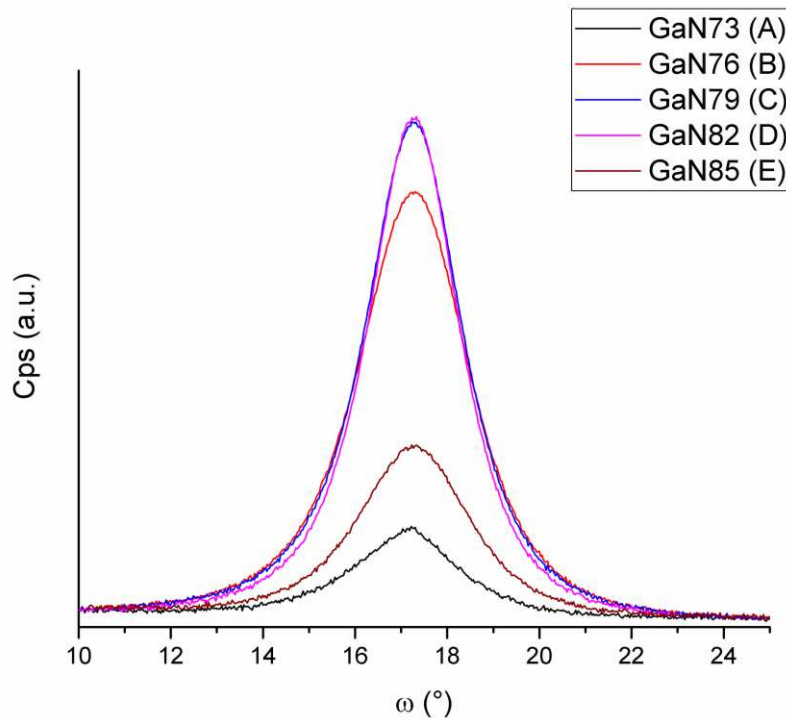


Figure 3. 6 ω scans of GaN grown using e--beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e).

Sample	Ga e-beam current (mA)	(002) FWHM peak from 2θ - ω pattern	(002) FWHM from ω pattern
A	73	0.51 ± 0.01	1.95 ± 0.01
B	76	0.1612 ± 0.0009	1.86 ± 0.01
C	79	0.1479 ± 0.0009	1.60 ± 0.01
D	82	0.1438 ± 0.0009	1.51 ± 0.01
E	85	0.275 ± 0.003	1.97 ± 0.01

Table 3. 3 Full-width-half-maximum values of GaN obtained from the fitting of (002) peak in 2θ - ω and ω scans

Finally, it is interesting to notice the difference between the FWHM values of these thin films obtained using HR-XRD in $2\theta-\omega$ and ω geometries (Table 3.3). Although in both cases when the e-beam current increases up to 82 mA an improvement of crystal quality is observed, a clear offset between the two trends is evident. Since the rocking curves are obtained by rotating the sample at different ω angles, while the detector is fixed, the FWHM values obtained using this geometry are considered more accurate and more reliable than the one obtained using $2\theta-\omega$ scan [127]. Therefore, from the values reported in Table 3.3 it can be concluded that the FWHM values obtained from the $2\theta-\omega$ scans are consistently underestimated. These results confirm the necessity to carefully choose the geometry in which the XRD experiment should be carried out in order to avoid misleading results or overestimation of thin film quality.

To further investigate the structural and microstructural properties of GaN thin films grown using e-beam PVD, cross-sectional TEM imaging was carried out. In Figure 3.7 BF TEM images taken along the $[1\bar{1}00]$ and $[11\bar{2}0]$ zone axes of all GaN thin films under study are shown. As expected, the thin film obtained using the lowest e-beam current (Figure 3.7 a-b) is made of small misoriented nanocrystallites alternated by small voids. These structural properties are in agreement with the AFM results discussed earlier in this chapter and with a rocking peak as large as $1.97 \pm 0.01^\circ$. As expected from growth rate results, when the e-beam current is increased the thin films become much thicker with thicknesses ranging between 160 and 184 nm. As shown in Figure 3.7 c-h, similar microstructures are observed in GaN thin films grown using e-beam currents ranging between 76 and 82 mA. All these thin films show columnar crystal structure normal to the surface of the substrate. In addition, triangular pits are visible between columns, as highlighted by the black arrows. These pits correspond to the holes observed in the AFM images and have already been observed in GaN thin films grown using N-rich conditions [145]. These pits have hexagonal pyramids shape and are usually generated by threading dislocations that terminate a few nanometres below the surface of the thin film (Figure 3.7 c-h, black arrows). The formation of these pits is believed to be related to the low mobility of Ga adatoms in N-rich conditions; while in Ga-rich conditions the adatoms diffuse to the most suitable site following 2D growth mechanism, which leads to smoother surfaces [145]. It is interesting to notice that when the highest Ga e-beam current, and therefore the highest III/V ratio, is used both these pits and the columnar structure are no longer visible (Figure 3.7 i-l). This different structure may indicate that when the e-beam current is as high as 85 mA the III/V ratio is high enough to promote the diffusion of Ga adatoms before they bond with nitrogen. These results would suggest that the GaN thin film obtained using the highest e-beam current is grown in Ga-rich conditions, in agreement with the lower growth rate reported in section 3.2. However, the AFM morphology of this GaN thin film did not suggest this type of regime and further investigation is necessary to clarify the conditions in which this sample was grown.

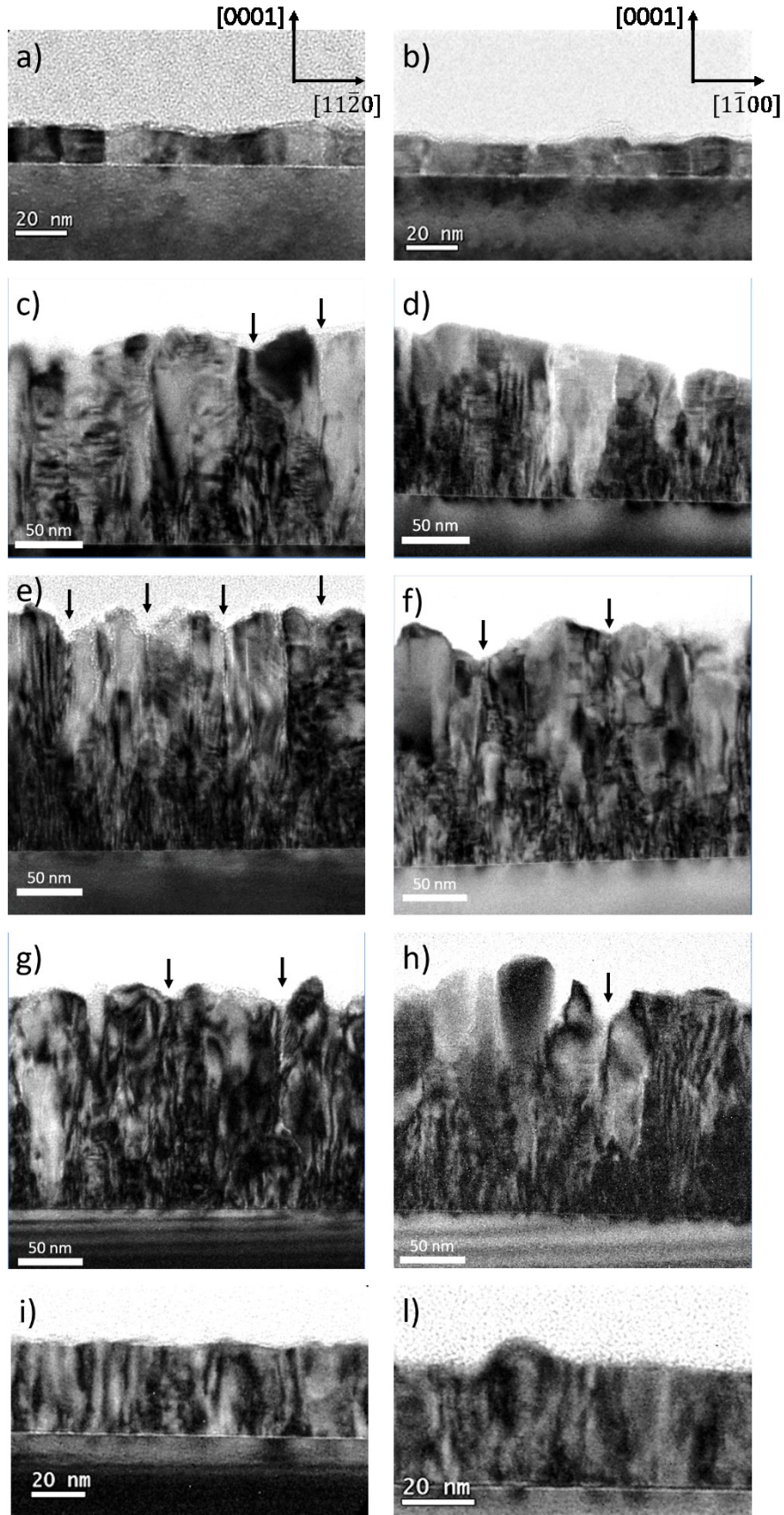


Figure 3. 7 Bright field TEM images obtained along the $[1\bar{1}00]$ and $[11\bar{2}0]$ zone axes, respectively, of GaN grown using e--beam current equal to 73 (a-b), 76 (c-d), 79 (e-f), 82 (g-h) and 85 mA (i-l). Black arrows were used to highlight the triangular pits present on the surfaces of GaN grown using intermediate e-beam currents (c-h).

High-resolution (HR) TEM imaging was also used to investigate the structural properties of the GaN thin films under study. In Figure 3.8 the low-magnification TEM images of the GaN samples taken along the $[11\bar{2}0]$ zone axis are shown; in addition, high-magnification images and diffraction patterns of the GaN/sapphire interfaces and the near-surface areas are shown in insets 1 and 2, respectively. As expected, the GaN grown using the lowest e-beam current (Figure 3.8 a) is highly defective, with high concentration of stacking faults and dislocations throughout the film. This high concentration of defects is probably due to the inefficient evaporation of Ga at this e-beam current and the resulting very slow growth rate (16 nm/h). When higher e-beam currents are used (Figure 3.8 b-d), relatively high concentrations of stacking faults parallel to the GaN/sapphire interface are still visible, as shown by the HR-TEM images and the elongated spots in the respective diffraction patterns. It is interesting to notice that while the long-range order is lost in multiple areas near the GaN/sapphire interface, lower concentrations of defects are visible in the near-surface area (Figure 3.8 insets 2), indicating an improvement of crystal quality during the growth. In addition, cubic inclusions are visible in some areas of GaN grown using intermediate e-beam currents. However, the concentration of this cubic phase is not high enough to be detected using HR-XRD, since no cubic-phase related peaks are visible in the $2\theta-\omega$ patterns (Figure 3.5 a-e). In addition, a relation between e-beam current and extension of cubic inclusions can be noted: when the e-beam current is 76 mA (Figure 3.8 b), the wurtzite structure is lost in large areas of the structure, however when the e-beam current is increased (Figure 3.8 c-d) the extension of the cubic inclusions progressively reduces. This reduction is in agreement with the rocking curve results reported in Figure 3.6, in which the FWHM gradually reduces when the e-beam current is increased from 76 to 82 mA, suggesting an improvement of crystal quality. Finally, when the e-beam current is as high as 85 mA (Figure 3.8 e) the columnar structure is no longer present, however high concentrations of stacking faults and dislocations are visible throughout the film. In all thin films under study these defects are visible along the $[11\bar{2}0]$ zone axis only and invisible along the $[1\bar{1}00]$ and the $[0002]$ zone axes (not shown); therefore the stacking fault observed in the GaN structures are believed to be I_2 stacking faults with displacement vector equal to $\frac{1}{3}\langle 10\bar{1}0 \rangle$, according to the invisibility criteria [105]. Further quantification of these structural defects in the structure, however, is beyond the scope of this work.

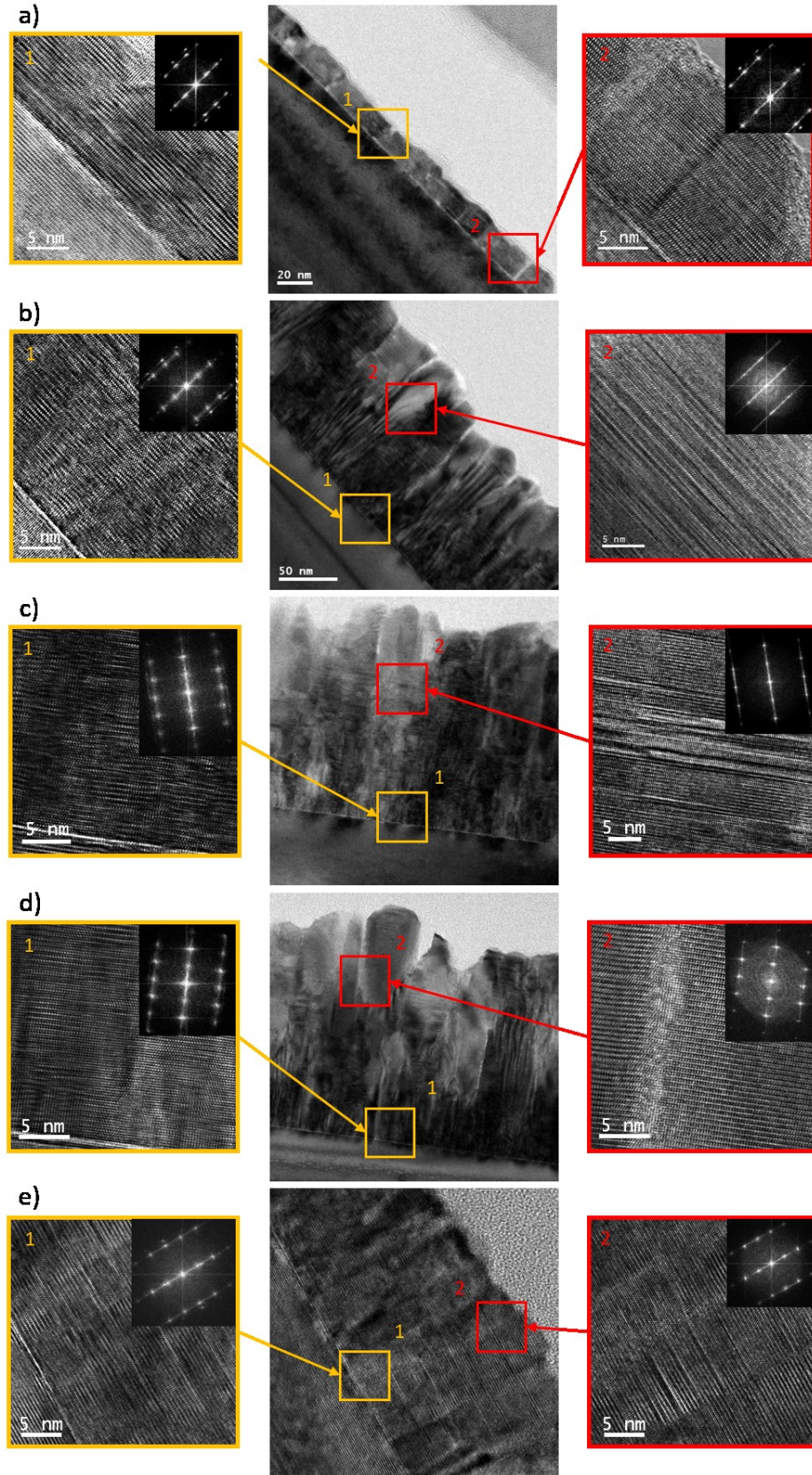


Figure 3. 8 High resolution TEM images taken along the $[11\bar{2}0]$ zone axis of GaN grown using e-beam current equal to 73 (a), 76 (b), 79 (c), 82 (d) and 85 mA (e). The red (1) and yellow (2) insets highlight the regions of the structure near the GaN/sapphire interfaces and the near-surface areas respectively.

Finally, the diffraction patterns obtained from the cross-section TEM images were used to calculate the c and a parameters of the GaN thin films. Since the absolute values of the lattice parameters obtained from the diffractions patterns suffer from a large calibration error, the c and a parameters obtained using this technique are generally considered unreliable. However, the c/a ratio is only affected by the experimental error arising from the correct aligning of the zone axis and not by calibration errors. Therefore, the calculation of the c/a ratio of a thin film can be used to evaluate the distortion and stress present in the structure. The c/a ratios of GaN thin films obtained using increasing e-beam current are plotted in Figure 3.9. All thin films under study have a c/a ratio much higher than the theoretical values of wurtzite GaN (1.6266 [148]), indicating that in all cases the wurtzite structure is highly distorted. Since GaN obtained using the lowest and highest e-beam current are only few tens of nanometres thick, the large c/a ratio might be due to some residual stress due to lattice mismatch with the underlying sapphire. The GaN thin films obtained using intermediate e-beam current, on the other hand, are largely thicker than the critical thickness and they are expected to be fully relaxed. Therefore, the larger c/a ratio of this thin film is believed to be related to relaxation strain necessary to accommodate the lattice mismatch between GaN and sapphire lattice parameters.

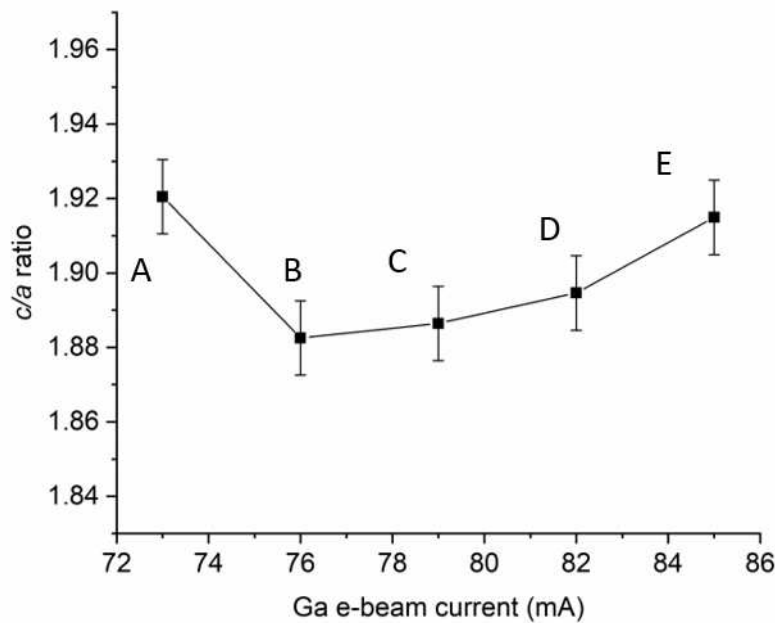


Figure 3. 9 c/a ratios obtained for TEM diffraction patterns of GaN grown using increasing Ga e-beam currents.

Since a comparison of structure distortions can only be made among thin films with similar thicknesses, only a comparison of c/a ratios among GaN obtained using intermediate e-beam currents can be carried out. The thin films obtained using lowest and highest e-beam current, in fact, are much thinner and therefore subjected to different degrees of strain; such that, a comparison with the rest of the dataset would not be reliable. From Figure 3.9 it is evident that when the e-beam current is tuned from 76 to 82 mA, an increment of c/a ratio is obtained. According to the c lattice parameters calculated

using HR-XRD, this increase of c/a ratio appears to be related to the elongation of the c lattice when the e-beam is increased. However, the reduction of the ratio could be also due to a decrease of the a parameter or a combination of longer c and shorter a parameters. Therefore, the direct measurement of a lattice parameter would be useful to better understand the trend of the c/a ratio for the thin films observed in Figure 3.9. This increment of the c/a ratio when the e-beam current is increased to 82 mA might be related to the density of defect present in the structure. From XRD and TEM results, in fact, it is evident that GaN grown using e-beam current equal to 82 mA shows much higher crystal quality than the rest of the samples. It is therefore possible that, while the structures of the other samples partially relax via generation of defects, the structure of GaN grown using 82 mA as Ga e-beam current remains strained, so that lower concentration of defects and more distorted wurtzite structure are obtained. Such that, the higher c/a ratio of Sample D is in agreement with an improvement of crystal quality consistently observed during this work.

3.5 Optical characterisation and band gap

The optical properties of GaN grown using e-beam PVD and their dependence on the used Ga e-beam currents are discussed in this section. In addition, the band gaps of these thin films are calculated using both the Tauc plot and photoluminescence spectra. The accurate determination of the band gap is of particular interest for GaN, since it determines the optical and electrical properties of the GaN-based final devices, such as LEDs or HEMTs.

3.5.1 Transmittance spectroscopy

Transmittance spectroscopy is a simple technique widely used to study the optical properties of thin films as well as liquids. The transmittance spectroscope is equipped with different lamps that can emit in a wide range of wavelength, usually between 200 and 800 nm or above. The photons emitted by these lamps interact with the sample and, depending on their energy and the properties of the material, they can be transmitted, adsorbed or reflected. Depending on the information needed, both transmittance and reflectance can be easily measured by changing the alignment of the instrument, while the absorbance is calculated using the formula $A = 1 - (T + R)$. In transmittance spectra the transmittance is usually high at large wavelengths, where the photons are less energetic, and drops at wavelengths close to the band gap of the material. This drop can then be used to extrapolate the band gap of the thin film under study, as described in detail in Chapter 2. In Figure 3.10 the transmittance spectra of GaN thin films grown using e-beam PVD are shown. GaN thin films grown using the lowest (Sample A) and highest (Sample E) e-beam currents have a smaller drop at shorter wavelength than the rest of the dataset. These results are probably due to the very thin thicknesses of these thin films: since both thin films are only few tens nanometres thick, the amount of GaN able to absorb light at these wavelengths is very small,

therefore the drop of transmittance is much smaller than that of the other thin films. GaN thin films grown using intermediate e-beam currents (Samples B-D), on the other hand, show an abrupt drop of transmitted light at wavelength about 390 nm, suggesting that the band gaps of these samples lie around 3.18 eV.

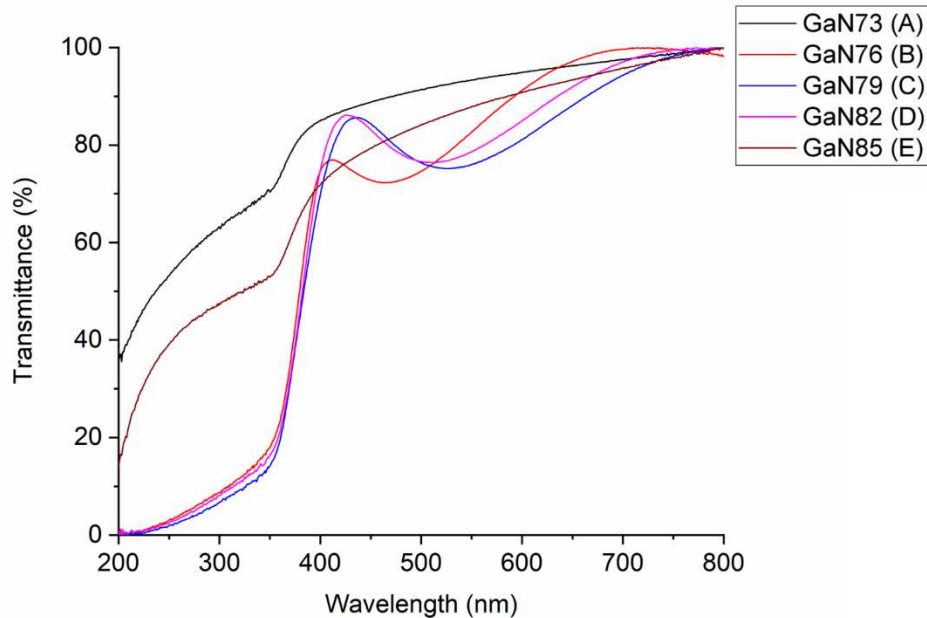


Figure 3. 10 Transmittance spectra of GaN grown using e-beam current equal to 73 (A), 76 (B), 79 (C), 82 (D) and 85 mA (E).

In addition, at larger wavelengths typical interference fringes are visible for Samples B – D. These interference fringes are generated by the internal reflections of light at the air/sample and sample/substrate interfaces and by their interference. The amplitude of the fringe is inversely related to the thickness of the thin film, and they are usually visible in thin films thicker than 100 nm with homogenous surfaces [149]. Interference fringes are visible only for GaN grown using intermediate e-beam currents (Samples B – D), while a straight line is observed when the lowest and highest e-beam currents are used. These fringes are often used to calculate several optical constants, such as absorption coefficient (α), both real and imaginary component of refractive index (refractive index n and extinction coefficient k), as well as the thickness of the thin film [150]. Different methods can be used to calculate these optical constants, such as iterative calculations [151], [152] or Swanepoel's method [149]. The maximum and minimum visible for all GaN grown using intermediate Ga e-beam current were used to calculate the refractive index according to Swanepoel's method [149]. In this case the refractive index s of the substrate must first be calculated by collecting the transmittance spectra of the substrate only. Then the transmittance of the maximum and the minimum of the fringe is used to calculate the refractive index according to the following equations:

$$N_1 = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (3.1)$$

$$n = [N_1 + (N_1^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \quad (3.2)$$

Where T_M and T_m are the transmittance of the maximum and the minimum of the fringe, respectively. The refractive index calculated for Sample B, C, and D are 2.08 ± 0.02 , 2.25 ± 0.02 and 2.22 ± 0.02 , respectively. These values are in good agreement with those reported in the literature [153], suggesting that GaN grown using e-beam PVD in N-rich conditions show relatively good optical quality.

Using the transmittance spectra shown in Figure 3.10, the Tauc plots of the GaN thin films were calculated and shown in Figure 3.11a. The Tauc plot is commonly used to extrapolate the band gap of thin films by plotting the product of the absorption coefficient α with the energy against the energy $h\nu$. In addition, the exponent of the product ($\alpha h\nu$) in the Tauc plot is determined by the nature of the band gap of the material. More detail about the calculation of the Tauc plot are reported in Chapter 2. In Figure 3.11a only the Tauc plot of GaN obtained using intermediate e-beam currents are shown, since Samples A and E were too thin to produce a reliable Tauc plot. In Figure 3.11b the extrapolated band gaps with the relative errors are plotted. Small change of band gaps is observed when the e-beam current is changed, however the variation of band gap is smaller than the error. This variation could be simply arising from experimental errors, such as measurement of the thickness using TEM or extrapolation of the linear portion of the Tauc curve. Such that, it can be concluded that no evident variation of band gap is observed in GaN thin films when the e-beam current is tuned from 76 to 82 mA.

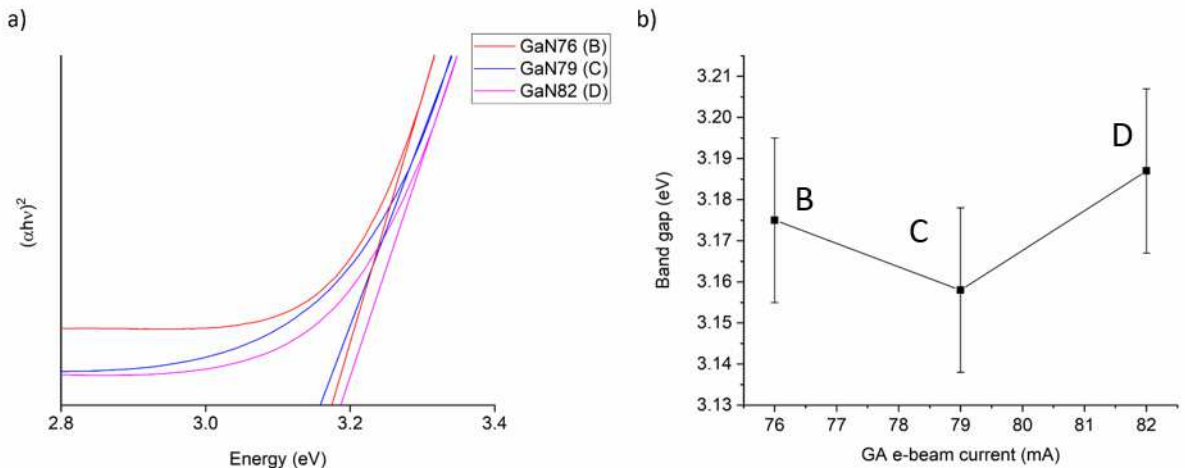


Figure 3. 11 Calculated Tauc plots (a) of GaN grown using e--beam current equal to 76 (B), 79 (C), 82 (D) and extrapolated band gaps (b).

The value of the band gaps obtained from the Tauc plot is estimated to be between 3.15 ± 0.02 and 3.19 ± 0.02 eV, which are much lower than the 3.4 eV reported in literature for GaN. It is possible that this narrower band gap is due to the thin thickness of the thin films, much smaller than that of bulk GaN

films usually a few micrometres thick. In addition, the presence of defects in the crystal structure could introduce localised states, resulting in band gaps much narrower than those reported for high-quality GaN grown using MOCVD. Further investigation of the band gap of these thin films was carried out using photoluminescence technique, as discussed in the following section.

3.5.2 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is another technique used to study the optical properties of thin films. Because of its advantages to be fast, non-destructive and contactless, this technique has recently become very popular for the evaluation of structural quality and defect concentrations in thin films. Photoluminescence is usually carried out either at room temperature (RT) or at low temperature (LT), where liquid helium is used.

The RT photoluminescence spectra of GaN thin films obtained using intermediate e-beam currents are shown in Figure 3.12a. All samples show similar PL spectra with a broad peak around 2 eV and a second peak centred about 3.10 eV. Convolution analysis was carried out to study number, position and relative intensity of the underlying peaks; the calculated peaks are shown in Figure 3.12a as bright green lines. The common yellow luminescence (YL) peak is present in all samples at 2 eV. This peak is usually related to the presence of structural defects that generate localised states in the band gap. These localised states reduce the energy transition of photons, giving rise to photoluminescence at low energy (1.5-2.5 eV) [154]. It is interesting to notice that the intensity of this broad peak decreases when the e-beam current increase. This reduced intensity is in agreement with a reduction of defect density in the structure and an improvement of crystal structure when the e-beam current is tuned from 76 to 82 mA.

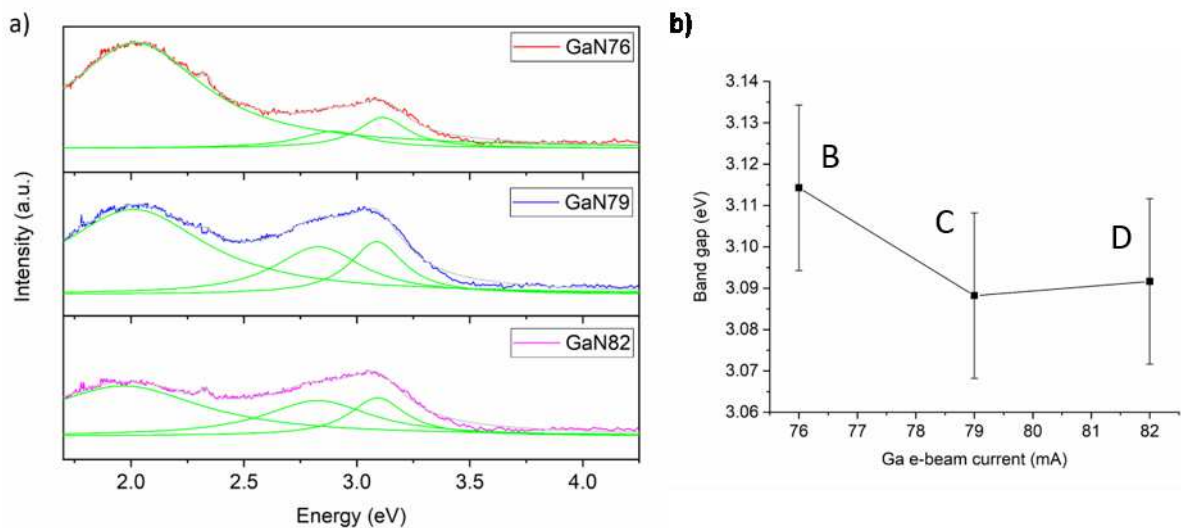


Figure 3. 12 Photoluminescence spectra (a) of GaN grown using e--beam current equal to 76 (B), 79 (C), 82 (D) and extrapolated band gaps (b).

Moving to higher energy, a peak at about 3.1 eV and a shoulder at 2.9 eV are observed in all samples. The more intense peak at 3.11 eV might be generated by the near-band edge excitation however it lies at energy much lower than the ones usually observed for GaN. This shift at lower energy is possibly due to the presence defects in the structure that introduce localised states in the band gap. The position of this peak was also used to evaluate the band gap of the thin films under study (Figure 3.12b). As expected from transmittance spectroscopy results, the values obtained of the GaN band gaps are lower than that usually reported in the literature. This red-shift of band gap to lower energy is possibly caused by structural defects in the structures that generated localised states in the band gap. In addition, the variation of band gap when the e-beam current increases is smaller than the experimental error. Therefore, it can be concluded that the band gap does not appear to change when the e-beam current is tuned from 76 to 82 mA, in agreement with transmittance results, and remains constant between 3.09 ± 0.02 and 3.11 ± 0.02 eV.

Finally, in all PL spectra a third peak can be observed at energy around 2.98 eV. The origin of this peak is not as clear as the others and can be generated by different type of interactions. It is possible that this peak is related to shallow donor bound excitations (DBE) generated by shallow donor states that lies just below that bottom of the conduction band [155]. Another explanation is that this peak is related to the recombination of excitations generated by either basal-plane or prismatic stacking faults present in the crystal structure [156]. In both cases, however, the generation of this peak can be attributed to the presence of structural defects in the structure. High concentrations of stacking faults are typically observed GaN thin films grown in N-rich conditions [105] and were confirmed by HR-TEM images discussed in Section 3.4.

3.6 Conclusions

In this chapter the structural and optical properties of GaN thin films grown in e-beam PVD system using increasing Ga e-beam current are presented. First the regime in which the growths take place was confirmed by both growth rate trend and AFM results. The dependence of growth rate on the Ga e-beam current used and the observed 3D morphology suggest that when the Ga e-beam current varies between 73 and 82 mA, GaN grows in N-rich conditions. The 3D morphology and the island nucleation mechanism were also confirmed using plan-view TEM imaging, in which misoriented, rounded nanocrystallites were observed. In addition, a strict relation between Ga e-beam current and crystal quality of GaN structure was observed. When the e-beam current is increased up to 82 mA, the size of the nanocrystallites increases, suggesting an improvement of crystal structure. This improvement was also confirmed using HR-XRD, in both $2\theta-\omega$ and ω scans, and cross-section TEM imaging. All results reported in this chapter, in fact, consistently suggest that when the Ga e-beam current is equal to 82 mA the optimum thin film is obtained. This sample, in fact, showed the largest nanocrystallites, the narrowest rocking curve and the lowest concentration of defects in HR-TEM images. If lower or higher

e-beam currents were used, a net drop of crystal quality was observed. Nevertheless, further optimization of the growth conditions is still necessary, since even the optimum thin films misorientations were still observed and the FWHM of the rocking curve was still of the order of 1° . In addition, the band gaps of these thin films were calculated using both Tauc plots and photoluminescence spectra. A band gap as narrow as 3.1 ± 0.2 eV was calculated for all thin films grown using intermediated e-beam currents and no sensitive variation was observed when the e-beam current was increased. Compared with the band gaps reported in literature, GaN grown using e-beam PVD show narrower band gaps. It is possible that this result is due to the thinner thickness of these thin films, compared with μm -thick GaN substrates. In addition, the narrower band gap might be caused by the presence of defects in the structure that generates localised states within the band gap. This interpretation was also confirmed by the photoluminescence spectra registered for these thin films. In photoluminescence spectra a relatively intense yellow-luminescence peak was observed in all sample. In addition, it was noticed that the intensity of this band decreases when the e-beam current increases, suggesting an improvement of crystal quality.

From these results it can be concluded that epitaxial GaN thin films can be grown using e-beam PVD and 82 mA appears to be the optimal e-beam current when the growth takes place in N-rich conditions. However, further optimisation is necessary to obtain thin films with crystal quality comparable to more-established growth techniques such as MOCVD. According to the results showed later in this thesis, in fact, GaN thin films showing much improved quality can be obtained after further optimisation of the e-beam PVD system. The uncertain conditions in which sample E (Ga e-beam current 85 mA) has been grown, for instance, is a clear evidence that the system was, at this point, not completely stable yet. However, as shown in Chapter 5, within this thesis work, the growth conditions and system have been much optimised and GaN thin film with largely improved properties has been obtained. Such that, the structural, optical and electrical properties of optimised GaN thin films grown using e-beam PVD are discussed further in Chapter 5.

Chapter 4

Characterisation of ScGaN

4.1 Introduction

In this chapter the structural and optical properties of ScGaN thin films grown using electron-beam physical vapour deposition (e-beam PVD) are investigated. Since the binary compounds GaN and ScN are stable in two different structures, wurtzite and rock-salt respectively, the structural properties of ScGaN thin films strictly depend on the concentration of scandium. From theoretical calculations, Constantin et al. [68] predicted that ScGaN remains stable in the wurtzite structure when the scandium concentration is lower than 27 %. Moreover, Tsui et al. [157] found that ScGaN grown using molecular beam epitaxy (MBE) remains stable in the wurtzite structure for scandium contents up to 26 %, while for higher concentrations, rock-salt inclusions were observed. In addition, Zhang et al. [32] calculated that the band gaps of ScGaN changes when the scandium content changes and increases for increasing scandium concentration up to 50 %. Therefore, in this chapter the structural and optical properties of ScGaN grown using e-beam PVD are investigated using a range of characterisation techniques: AFM, XRD, TEM and UV-visible spectroscopy. In addition, the dependencies of these properties on the concentration of scandium are also studied and discussed in the following chapter.

4.2 Growth rate

The growth rate is a crucial parameter for the deposition of thin films, and its fine control is necessary to obtain high-quality thin films with reproducible properties and thicknesses. Generally, the growth rate of nitride thin films depends on several conditions, such as substrate temperature (T_{sub}), nitrogen partial pressure (p_{N_2}) and III/V ratio in the chamber. For example, it was found that for InGaN the growth rate is largely dependent on the substrate temperature and decreases when the substrate temperature increases [158]. In addition, the growth rate changes when the ratio between the III and V materials in the chamber changes. In binary GaN growth, when the III/V ratio is very high the growth takes place in Ga-rich regimes. In this case the growth rate is limited by the availability of nitrogen nearby the substrate surface and it remains constant even when the Ga e-beam current is increased. On the other hand, when III/V ratios are very low, the growth rate is limited by the concentration of Ga adatoms on the surface of the substrates, therefore small changes of Ga e-beam currents lead to large variations of the growth rate. Different III/V ratios result in different morphological and structural properties, and a careful monitoring of this ratio is necessary to obtain the desired properties.

However, for ScGaN thin films the dependence of growth rate on the III/V ratios is much more complex and the growth rate of ScGaN thin films with different concentration of Sc are reported in Figure 4.1 and Table 4.1. In addition to the presence of a third Sc-rich regime, it was found that the growth rate largely changes when the Sc e-beam current increases, while all the other conditions remain constant. As reported in Table 4.1, in these growth conditions when Sc is not evaporated and binary GaN is grown, the growth rate is exceptionally slow and even after 5 hours of growth the GaN thin film is only 40 nm thick. The slow growth rate of GaN is probably a consequence of the high temperature of the substrate during the growth (850 °C). Heying et al. [145] reported that when the surface of the substrate is heated at temperature higher than 800 °C the growth rate of GaN tends to decrease. This decrease is probably due to the desorption of reactive species from the substrate, as well as the decomposition of precursors [145]. However, when scandium is introduced in the system, the growth rate increases substantially, regardless of the high substrate temperature. As shown in Figure 4.1, the growth rate increases from 8 (Sample A) to 40 nm/h (Sample B) when the Sc/Ga e-beam current ratio increases from 0 to 0.25, and it is as high as 334 nm/h for the highest Sc/Ga ratios, equal to 0.375 (Sample E).

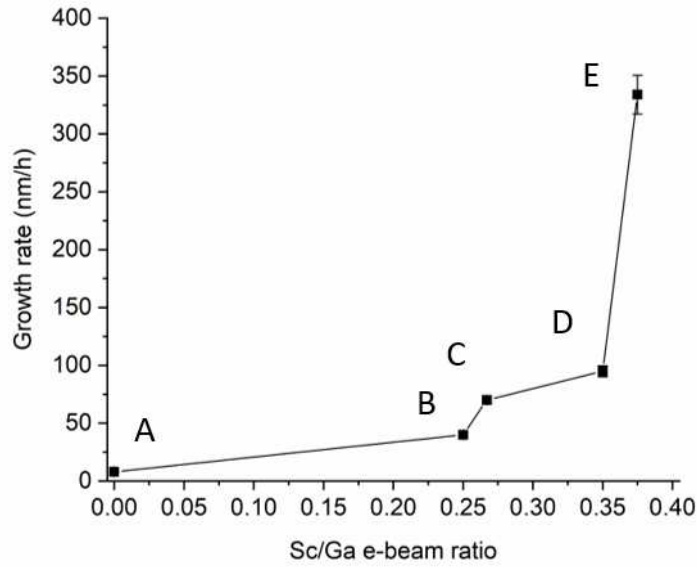


Figure 4. 1 Plot of growth rate vs of Sc/Ga e-Beam current ratio. The substrates were all heated at 850 °C and the p_{N_2} is maintained at 1×10^{-4} tor.

Sample	Sc/Ga e-Beam ratio	Estimated Sc content	Growth time (min)	Thickness (nm)	Growth rate (nm/h)
A	0	0	300	40	8
B	0.25	0.02	30	20	40
C	0.267	0.05	30	35	70
D	0.35	0.15	60	95	95
E	0.375	0.20	30	167	334

Table 4. 1 In the table the Sc/Ga e-Beam ratio, the estimated scandium content and the growth rate for all samples are reported.

This increase in the growth rate when the Sc/Ga ratios increase, while all the other growth conditions remain constant, is probably related to the interaction of Sc with molecular nitrogen present in the chamber. It is known that when Sc is present in the growth chamber it tends to catalytically decompose molecular N_2 in reactive nitrogen [159]; therefore, when Sc is present near the surface of the substrate, a higher concentration of nitrogen is available for the growth of ScGaN thin films. As a consequence, the growth rate quickly increases when the Sc e-beam current is increased, leading to a ScGaN thin film 167 nm thick after only 30 minutes of growth when the highest concentration of Sc is used (Sample E). Increases in the growth rate when the Sc concentration was increased have also been observed in ScGaN grown using plasma-enhanced MBE [157], in agreement with the results reported in this thesis. This catalytic reaction between Sc and molecular N_2 , however, alters the III/V ratio during the growth of ScGaN thin films, therefore it is difficult to predict *a priori* if the growth takes place in Ga- Sc- or nitrogen-rich conditions. Hence, the determination of the growth regime in which the ScGaN thin films have been grown must be done by comparing ScGaN results with GaN and ScGaN properties reported in literature, using different characterisation techniques, as discussed in the following sections.

4.3 Determination of Sc concentration

The determination of composition of ternary thin films is fundamental to understand the properties of the material and to study how they change when the relative concentrations of elements change. In the case of ScGa₂N, for instance, the structural properties strictly depend on the concentration of Sc: since ScN and GaN are stable in different structures, ScGa₂N is expected to be stable in wurtzite, wurtzite-like or rock-salt structures depending on the relative concentration of Sc and Ga. In addition, it has been predicted that the band gap increases when the Sc concentration increases. Therefore, it is important to relate the optical properties to the Sc content accurately, in order to fine-tune the properties of the final ScGa₂N thin film.

For the thin films grown using e-beam PVD, the ratio between the e-beam currents of two metals is a useful tool to estimate *a priori* the content of the thin film. The e-beam current ratios used in this work and the estimated concentrations of Sc are reported in Table 4.1. However, it is still necessary to confirm the exact concentration of scandium and its homogeneity throughout the film, using *ex situ* techniques. However, the *ex-situ* determination of Sc in ScGa₂N is not trivial, since the techniques commonly used to determinate the composition of thin films are not suitable in this case. Generally, the composition of thin films is calculated using TEM- or SEM-EDX (energy dispersive X-rays): using this technique the relative concentrations of elements is calculated using the relative intensity of the characteristic X-ray emission peaks. However, the $L_{\alpha 1}$ peak of scandium and the $K_{\alpha 1}$ peak of nitrogen lie respectively at 0.395 keV and 0.392 keV [160], overlapping. Sc peaks at higher energy may be used; however, the very low intensities of these peaks increase the detection limit and make the composition determination not accurate for these thin films [109]. X-ray photoelectron spectroscopy (XPS) is another surface-sensitive technique widely used to determine the composition of thin films. In this case the composition of thin films is obtained by analysing the relative areas of binding energy peaks of different elements. However, in the case of ScGa₂N the binding energy of Sc2*p*, N1*s* and the Ga Auger peaks lie very close to each other within a range of only 10 eV [161]. The overlapping of these peaks makes the quantification of Sc challenging and underestimations of the real Sc concentration were observed when XPS was used [162].

For these reasons, the compositions of ScGa₂N thin films studied in this work were obtained using secondary ion mass spectroscopy (SIMS). This technique is useful not only for the composition determination, but also for the evaluation of composition homogeneity and impurity levels throughout the thin film with a detection limit of ppm. Typical positive and negative depth profiles of GaN grown using metalorganic chemical vapour deposition (MOCVD) are illustrated in Figure 4.2a and b, respectively. In order to enhance the sensitivity and improve the detection limits of the analysis, oxygen (O_2^+) primary sputtering gun was used. However, even when the energy of the gun was as low as 500 eV, the counts of Ga⁺ were too high and above the saturation limits. Therefore, a 1000 eV caesium (Cs⁺) gun was used as primary sputtering gun for all samples.

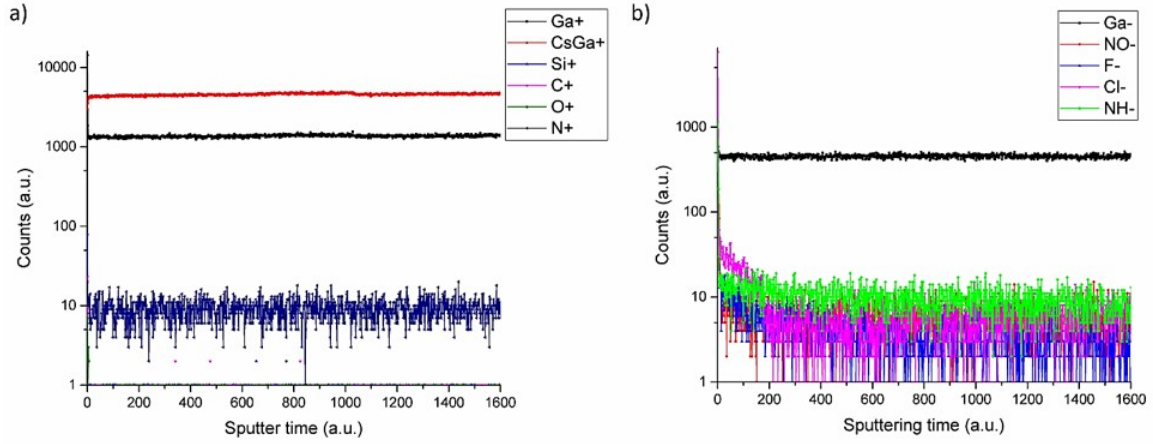


Figure 4. 2 SIMS depth profile with positive (a) and negative (b) polarity of GaN thin film grown using MOCVD.

The depth profiles of GaN and ScGaN samples obtained using positive polarity are illustrated in Figure 4.3. Using GaN grown in MOCVD system as reference, the levels of common impurities such as silicon, carbon and oxygen can be studied for both GaN and ScGaN grown using e-beam PVD.

While the carbon levels are below the SIMS detection limit for all the thin films studied, both silicon and oxygen levels in PVD-GaN are between 1 and 10 counts/s. This larger inclusion of silicon and oxygen in PVD-GaN might be due to several factors. First, since the growth of GaN takes place at high temperature (850 °C), the growth rate of this thin film is exceptionally slow and equal to 4 nm/h. Slow growths usually favours the inclusions of impurities such as silicon or oxygen and this might explain the SIMS results in Figure 4.3b. In addition, PVD-GaN is thinner than the other thin films under study and shows a very rough surface (see Section 4.4). Since PVD-GaN has a rough surface, larger amounts of dangling bonds are exposed to oxidation, generating the native oxide Ga_2O_3 on the surface [163].

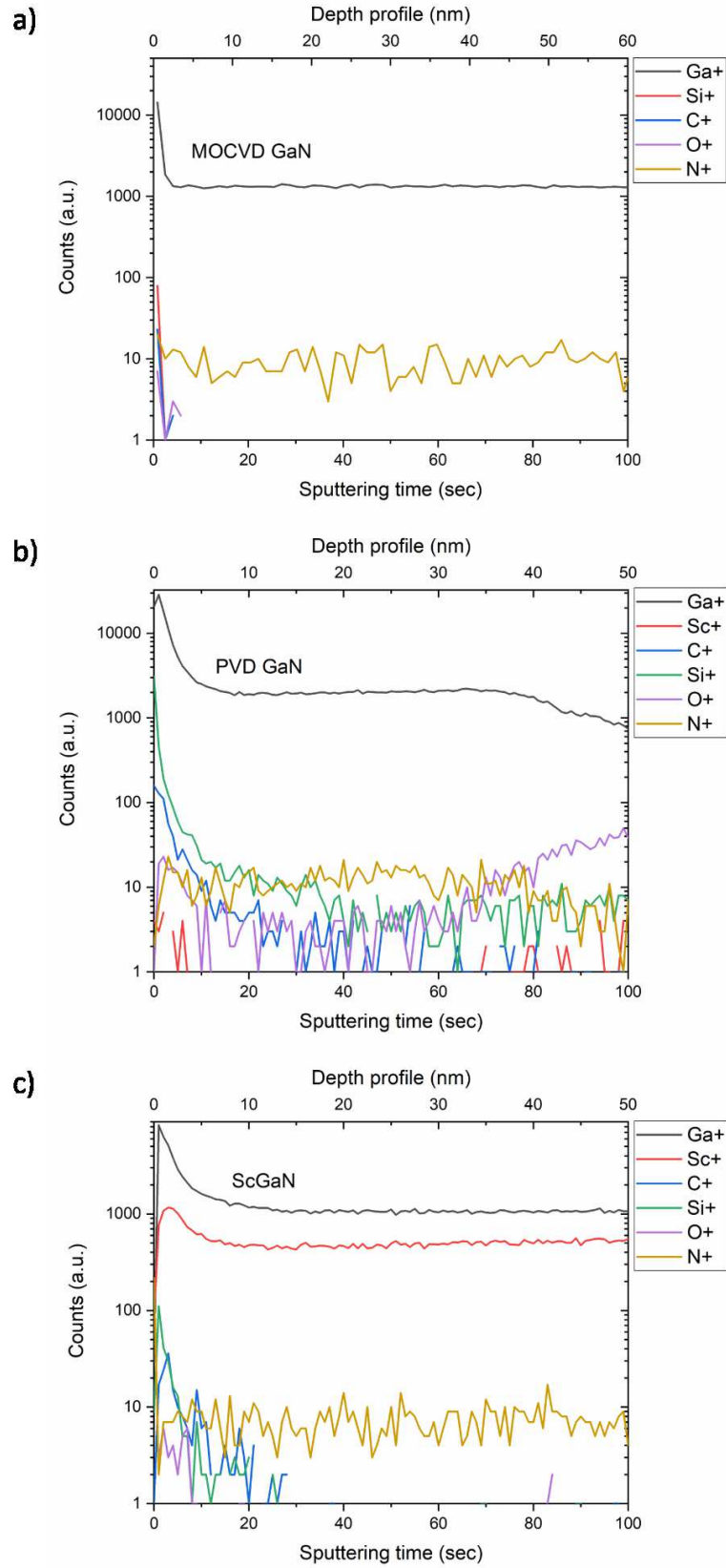


Figure 4. 3 SIMS depth profile with positive polarity of GaN grown using MOCVD (a) and e-beam PVD (b) and ScGaN grown using e-beam PVD (c). The spike levels of Ga+ and Sc+ registered at the first few seconds of the analysis are an artefact of the technique and visible in both e-beam PVD thin films, as well as the MOCVD GaN reference.

In addition, because of the rough surface, in this case a larger amount of SIMS data come from the surface of the thin film, as schematically shown in Figure 4.4, which further increases the level of oxygen impurities. The further increase of oxygen for sputtering time higher than 90 sec comes from the sapphire used as a substrate. Regarding the impurities levels of PVD-ScGa_N, those appear to be comparable to MOCVD-GaN, suggesting that no detectable impurity incorporation takes place during the growth of these thin films in the PVD system. It is also interesting to notice that the N⁺ levels for all e-beam PVD samples are comparable to the MOCVD GaN, suggesting that the nitrogen partial pressures used to grow these materials lead to stoichiometric nitride thin films.

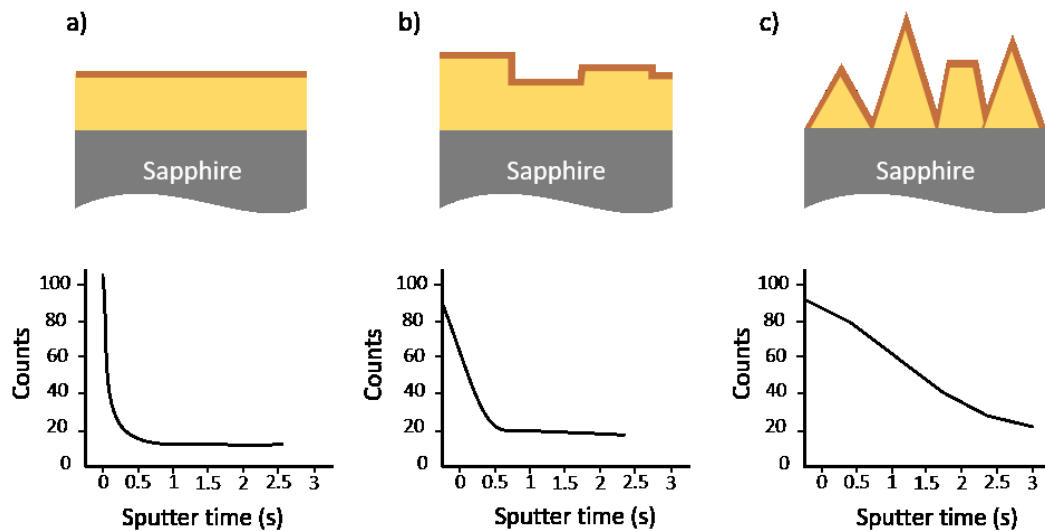


Figure 4. 4 Simplified representation of the relation between amount of exposed surface and SIMS depth profile of surface impurities, such as oxygen or silicon.

As shown in Figure 4.3, the depth profiles obtained using SIMS are generally expressed in absolute quantities, such as sputtering times and counts. Since the analysis can be influenced by matrix effects as well as experimental variables, high-quality standards are usually used to convert absolute counts in concentration or percentages of the elements in the thin films. Since ScGa_N standards are not yet available, high quality GaN grown using MOCVD is used as standard to calculate the content of the thin films following the method reported in ref. [164]. In addition, the sputter time is converted in sputtering depth using a Dektak profilometer. In Figure 4.5 and Table 4.2, the Ga and Sc concentrations of ScGa_N (Sample D and E) grown using e-beam PVD are reported. The determination of Sc was unfortunately not possible for Samples B and C: high levels of interference from aluminium and oxygen coming from the sapphire substrates made not possible the quantification of elements in these thin films. These interferences are possibly due to the very low thickness and roughness of these thin films.

It is interesting to notice that the SIMS results reported in Figure 4.5 and Table 4.2 are in good agreement with the *a priori* estimations based on the e-beam current ratios. The concentration of scandium remains homogeneous throughout the film in both samples and no scandium accumulation layer on the surface (Figure 4.5) or nucleation layer near the sapphire surface (not shown) are observed.

These results suggest that a homogenous growth with good control of the evaporation of materials can be achieved when e-beam PVD is used as growth technique.

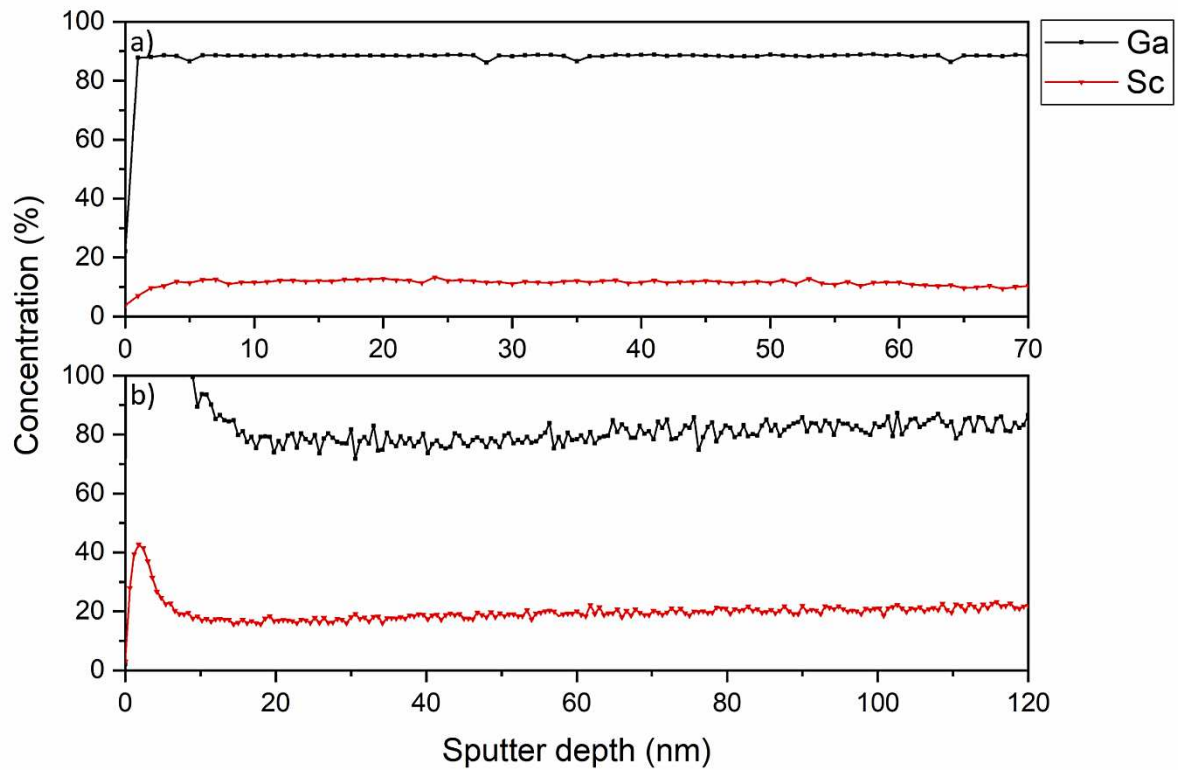


Figure 4. 5 Depth profiles of ScGaN thin films of Sample D (a) and E (b) expressed as a function of Ga and Sc percentages vs sputtering depth. The spike levels of Ga⁺ and Sc⁺ registered at the first few seconds of the analysis are an artefact of the technique and visible in both e-beam PVD thin films, as well as the MOCVD GaN reference.

Sample	Sc content from Sc/Ga e-Beam ratio	Sc content form SIMS
D	0.15	0.12 ± 0.02
E	0.20	0.20 ± 0.02

Table 4. 2 Concentrations of Sc in ScGaN samples as estimated from the Sc/Ga e-beam ratio and from the SIMS depth profiles.

Low-resolution scanning transmission electron microscopy (LR-STEM) was used to investigate further the homogeneity of scandium within the thin films. In Figure 4.6 the STEM images of Samples D and E are shown. In both cases no evident contrast that can be related to Sc accumulation layers and no compositional segregation can be observed. Therefore, ScGaN thin films grown using e-beam PVD in these growth conditions show uniform composition along the whole thickness without evident cubic inclusions or accumulation layers.

The contrast observed in the Figures 4.6 a and b is more likely to be related to strain present in the thin films; however, due to the large enhancement of the growth rate when the scandium concentration increases, it is difficult to relate the strain present in the thin films with its scandium content. This relation will be further discussed later in this chapter.

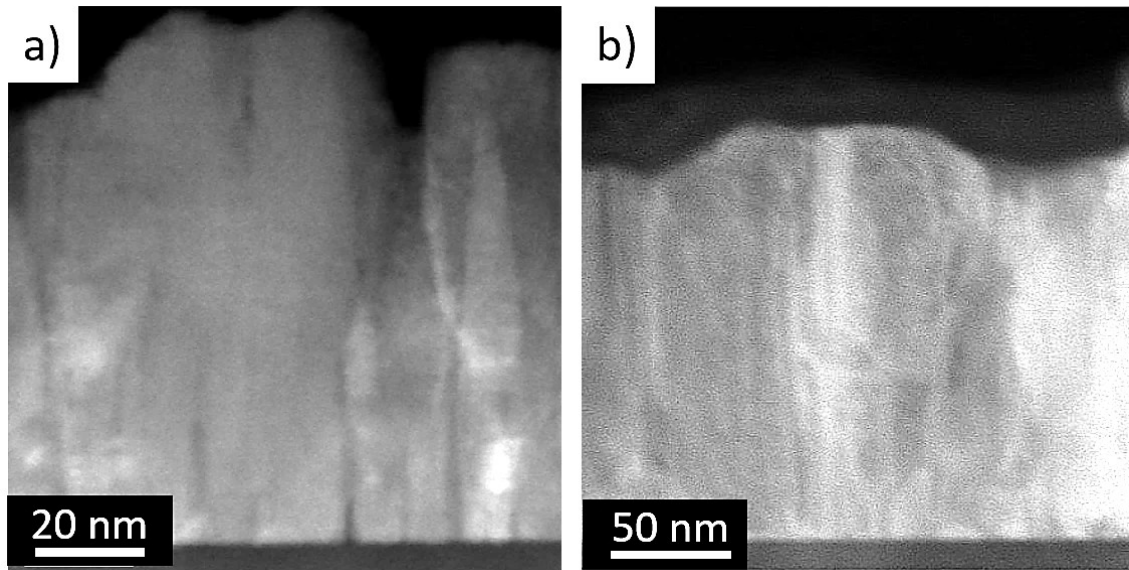


Figure 4. 6 STEM-HAADF images taken at the $11\bar{2}0$ zone axis of $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ with x equal to 0.012 (a), 0.20 (b), showing no evident composition segregation.

4.4 Surface morphology

Atomic force microscopy (AFM) has been used to study the morphology of ScGaN thin films grown using e-beam PVD. In Figure 4.7 the 2D AFM images of GaN and ScGaN with different Sc concentration are shown. All films show a compact rough surface made of rounded nanocrystallites nucleated following a 3D growth mechanism. The 3D rounded-nanocrystallite morphology has already been observed for MnGaN [165] and ScGaN [109] grown using MBE technique, and it usually suggests that the growth takes place either in N-rich or Ga-poor Metal-rich conditions. If, in fact, the concentration of nitrogen near the surface of the growing thin film is very high, the reaction of Ga and Sc adatoms to deposit ScGaN is much faster than the diffusion to proper sites [105]. Therefore, the deposition of GaN and ScGaN nanocrystallites is faster than the adatom diffusion and a 3D island growth is obtained. While the rounded-nanocrystallite morphology is evident for all scandium contents, a trend in roughness and nanocrystallite size is observed (Figure 4.8a and b). For intermediate scandium content, the nanocrystallites start to coalesce generating more compact well-rounded nanocrystallites (sample C), which finally fuse in flatter nanoclusters when the scandium content further increases (sample E). A similar trend was observed in MnGaN growth, and might suggest that when the Sc concentration increases, the growth regime shifts from N-rich to Ga-poor Metal-rich conditions [165]. When the Sc/N ratio increases near the surface of the growing film, Sc atoms might adsorb on the surface so that the accumulation of N atoms is prevented. The presence of higher concentration of Sc on the surface facilitates the diffusion of adatoms before reacting, so that smoother surfaces and bigger nanocrystallites can be obtained, as shown in Figure 4.8a and b.

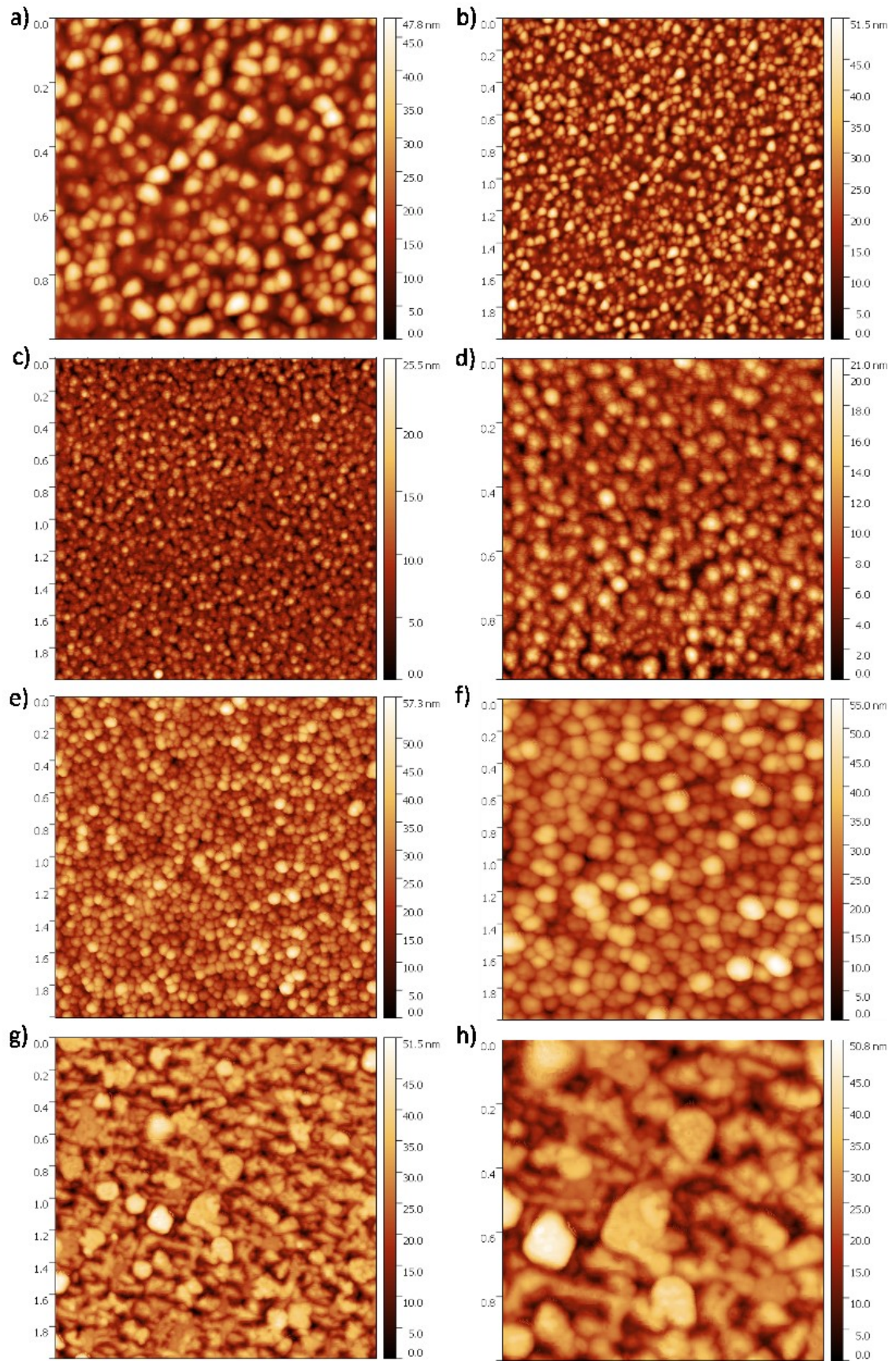


Figure 4. 7 2x2 μm² and 1x1 μm² AFM height images of GaN (a-b) and Sc_xGa_{1-x}N with x equal to 0.02 (c-d), 0.12 (e-f) and 0.20 (g-h). All the images are processed using parabolic flattening.

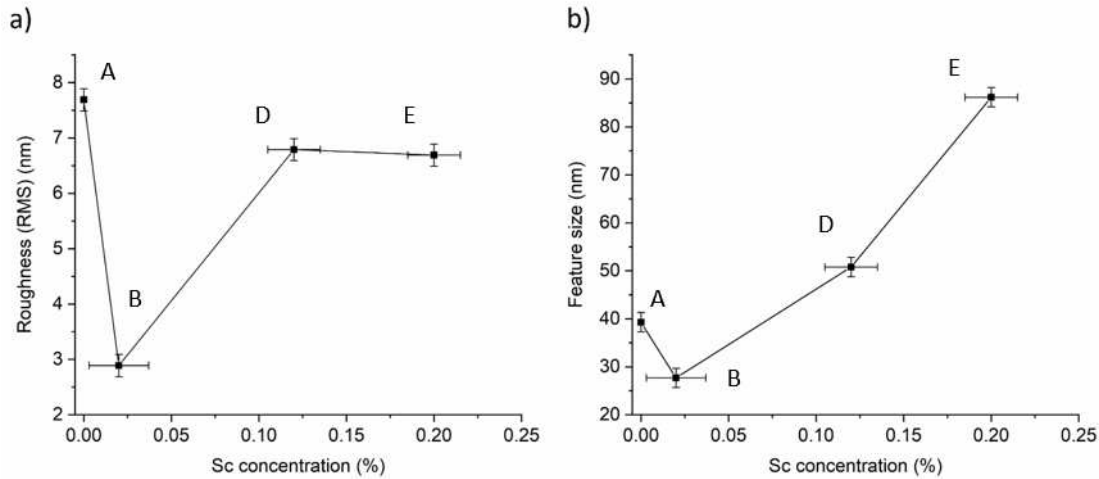


Figure 4.8 Root-mean-square (RMS) (a) and nanocrystal size (b) values for GaN and ScGa_N thin films extrapolated from AFM data.

It is also possible that the increment in nanocrystallite size is related to an improvement of crystal quality when the concentration of Sc is increased. This improvement of crystallinity in ScGa_N with higher concentration of Sc might be due to different factors. First, it is possible that the improved crystallinity is related to the high substrate temperatures used during the growth. Moram et al. [159] suggested 850 °C as optimal growth temperature for binary ScN, while GaN is usually grown at temperatures between 600 and 800 °C. Therefore, it is expected that ScGa_N shows improved crystal quality at these temperatures compared to binary GaN. Another possible explanation is that the higher thicknesses or the faster growth rates of these samples (D and E) lead to improved crystal quality; however, the improvement of crystal quality might be directly related to the higher concentration of Sc in the structure. This relation will be further studied in Section 4.5.

4.5 Structural and microstructural characterisation

The large band gap and exceptionally high piezoelectric constant of ScGa_N have attracted increasing attention for possible application of this scandium-based material in high electron mobility transistors (HEMTs). In this class of device, the channel is generated at the interface between GaN (buffer layer) and AlGa_N (active layer) grown above it. The band offset of AlGa_N/GaN structure generates a deep quantum well in which electrons are physically confined and show very high mobility. However, mobility and concentration of these electrons strictly depend on the crystal quality of AlGa_N layer, since defects in the layer are believed to act as traps that lower the performance of the device. Therefore, to successfully use ScGa_N as alternative active layer, a comprehensive study of its structural properties and their dependence on Sc concentration must first be carried out.

In this work, the structural and microstructural properties, as well as the nature of defects, in ScGa_N thin films are fully characterized using HR-XRD, TEM and HR-STEM techniques.

Since these ScGaN thin films are grown directly on sapphire without employing any buffer layer, HR-XRD in $2\theta-\omega$ and ω modes can be used to calculate the c parameter of the wurtzite structures and to evaluate the quality of the crystal structure. The $2\theta-\omega$ HR-XRD patterns of GaN and ScGaN thin films with increasing scandium content are shown in Figures 4.9, while the positions of (002) peak of ScGaN and the calculated c parameters are summarized in Table 4.3.

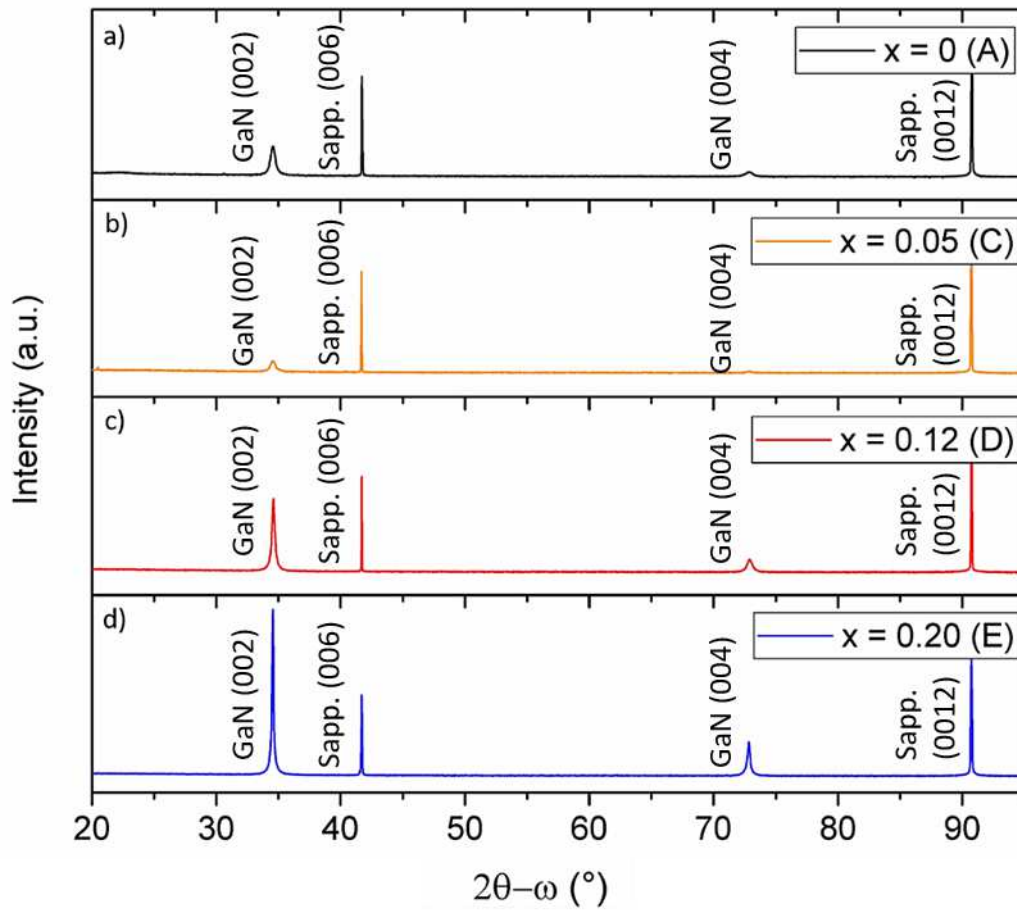


Figure 4. 9 $2\theta-\omega$ scan of GaN (sample A) (a) and ScGaN thin films with different Sc concentrations (samples C-E) (b-d).

Since the HR-XRD analysis is carried out in symmetric geometry, only the (00x) peaks are visible and only the c parameter can be calculated. As shown from the HR-XRD overall patterns (Figure 4.9), both the (002) and (004) peaks are evident for all films. The presence of only these peaks confirms that the epitaxial growth along the [001] preferential direction is achieved for all samples grown using e-Beam PVD technique, while no secondary phases are evident in any of the samples. From theoretical results an increase of lattice parameter was expected when Sc concentration is increased in ScGaN samples. However, from the values reported in Table 4.3, the lattice parameter c first decreases when the scandium content increases from 0 to 5 % and 12 % and then increases again and become slightly larger than GaN for the highest concentration of Sc. The reduction of lattice c suggests that in ScGaN with intermediate concentration of Sc tensile out-of-plane stress might be reduced and similar trend was

observed in Raman results discussed later in this chapter. However, the strict dependence of growth rate, and in turn thickness of the thin film, to the Sc concentration makes difficult to directly compare the stress levels in these thin films. Future investigation of the lattice parameters of these thin films grown with similar thicknesses will be helpful to better understand the stress present in these thin films.

Sample	Sc content	$2\theta-\omega_{002}$	c lattice parameter	Out of plane strain $\left(\frac{c_{exp}-c_{ideal}}{c_{ideal}}\right)$
A	0	34.5272	5.1913 ± 0.0002	+ 0.0012
C	0.05 ± 0.03	34.5631	5.18602 ± 0.00004	+ 0.0002
D	0.12 ± 0.02	34.5709	5.1849 ± 0.0001	- 0.00004
E	0.20 ± 0.02	34.5263	5.1914 ± 0.0002	+ 0.0012

Table 4. 3 (002) peak positions and calculated c lattice parameters and calculated strain level are reported for ScGaN with increasing concentration of scandium.

In addition to the peak position, in Figure 4.9 it can be noticed that the intensities of the (002) peak largely change when the scandium content is changed, and it is substantially higher for sample E. This increase in intensity could be due to a thickness effect, since sample E is also the thickest sample in the set; however, it is also possible that higher content of scandium can somehow lead to higher-quality crystal structures.

To investigate further this relation between peak intensity and scandium content, ω pattern, or rocking curves, are performed and shown in Figure 4.10 together with the respective full width at half maximum values (FWHM). In agreement with the intensity trend in $2\theta-\omega$ scan, both GaN and ScGaN with lower concentration of Sc have a FWHM higher than 1° , which suggests that in both case high concentrations of in-plane rotations are present and the film is not single crystal. ScGaN with higher concentration of Sc (Sample E), on the other hand, shows a much sharper and more intense peak with a FWHM as low as 0.435° , which indicates a high-quality single crystal structure. Although the great non-linear influence of scandium concentration on the growth rate of ScGaN might introduce some thickness off-set, these results should be still relevant for the evaluation of the crystal quality of ScGaN thin films when the scandium content is increased. In rocking curve scans, in fact, the detector is fixed at a specific Bragg reflection while the sample is tilted around the same reflection, so that the FWHM obtained is mainly dependent on the distribution of nanocrystallite misorientations and it is mostly independent of the thickness of the thin film. In addition, although in this set the thickness increases almost linearly with the scandium content, there is no clear trend either in intensity or width of the peaks that might suggest a relevant off-set. Therefore, these rocking curve results suggest that, for the specific concentration of scandium present in sample E, the crystal quality greatly increases and the FWHM drops down to 0.435° .

If compared with ScGaN and GaN grown using different techniques [162], [166],[166], [167][164], [165] FWHM value of sample E is quite remarkable, especially if one considers that this thin film is only 167 nm thick and grown directly on sapphire without using any buffer layer. This marked increase in crystal quality for this specific scandium content could be due to several factors. One possible

explanation is that in sample E there is an unexpected relation between ScGa₂N and sapphire lattice parameters that leads to a relaxation of the structure and a reduction of point and planar defect concentrations within the film or at the interface with the substrate. This improved crystal quality in the ScGa₂N thin film with highest concentration of Sc (Sample E) suggested by both AFM and HR-XRD results, is also confirmed by the microstructural characterisation.

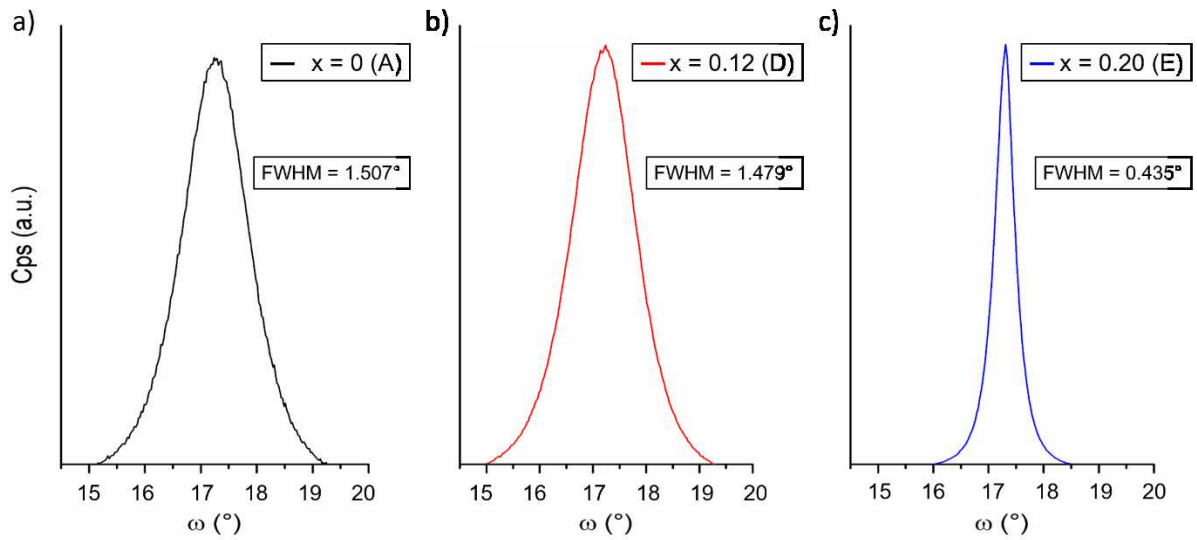


Figure 4.10 ω scan of GaN (sample A) (a) and ScGa₂N with 12 % (b) and 20 % (c) of Sc.

The influence of the Sc concentration on the microstructural properties of ScGa₂N thin films was studied using TEM, HR-TEM and HR-STEM. In Figure 4.11 the bright field (BF) TEM images taken along the $[11\bar{2}0]$ zone axis using an objective aperture 20 cm large are shown. GaN (Figure 4.11a) and ScGa₂N with lower concentration of Sc (Figure 4.11b) are made of small nanocrystallites, highly misoriented; in addition, in both cases a very rough surface is observed. These results are in agreement with both the AFM and HR-XRD results of these thin films and might be related to the very slow growth rate of these samples. When the scandium concentration is increased (Figure 4.11c) columnar structure and stacking faults are observed. However, when the Sc concentration is further increased (Figure 4.11d) the structure of the thin film drastically changes: neither the columnar structure nor the stacking faults are observed, suggesting an improvement of the crystal quality. These results are in agreement with AFM images, in which to an increment of Sc concentration correspond an increment of diffusion length of the adatoms.

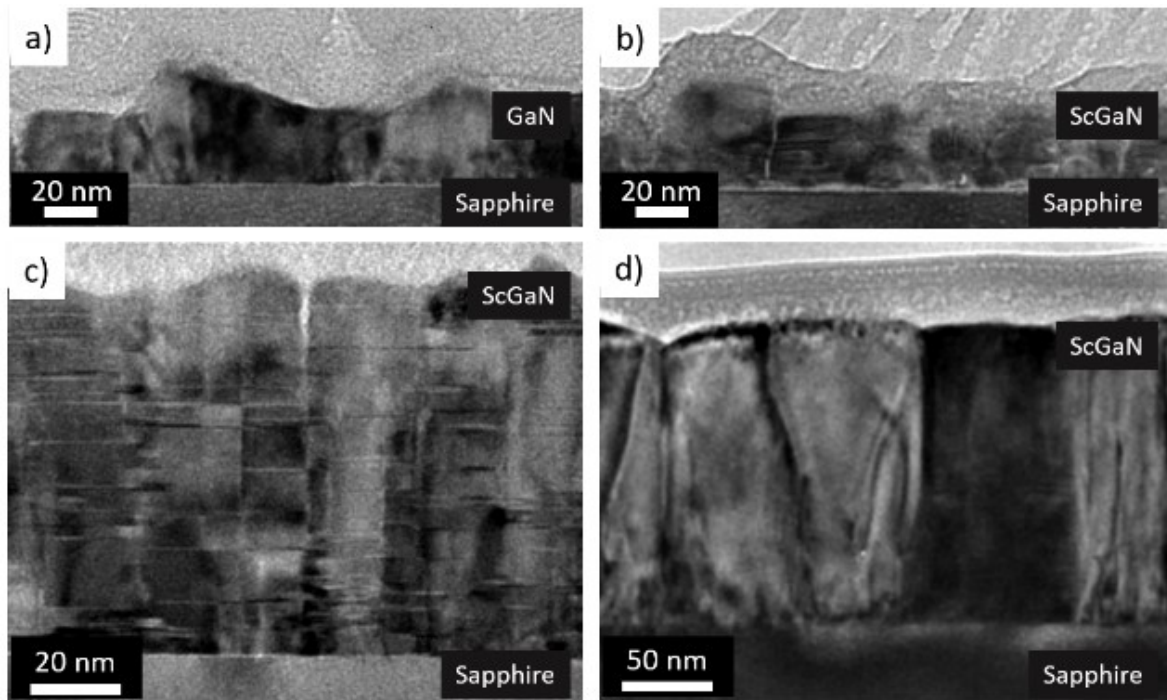


Figure 4.11 Bright field TEM images of GaN (a) and $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ with x equal to 0.05 (b), 0.12 (c) and 0.20 (d). The images are taken at the $11\bar{2}0$ zone axis using a 20-cm objective aperture.

HR-TEM images of GaN and ScGaN thin films were also obtained and shown in Figure 4.12. It is worth remarking on the quality of crystal structure of GaN (Figure 4.2a) at this magnification: although at a long distance the thin film is made of small, misoriented nanocrystallites, within the nanocrystallite the crystal quality is surprisingly high. This high crystal quality can be even observed at the interface with sapphire, where no disordered or amorphous nucleation layer is observed. The high quality of the thin film is confirmed by both the HR-TEM image (Figure 4.12a) and the respective diffraction pattern (Figure 4.12a inset 1 and 2). When a low content of Sc is introduced (Sample C), high concentrations of stacking faults are observed (Figure 4.12b). The presence of these defects is also confirmed by the elongate shapes of the diffraction spots (Figure 4.12b inset). When the Sc concentration is further increased (Sample D), stacking faults and dislocation along the c direction are observed in both bright field (Figure 4.11c) and HR-TEM (Figure 4.12c) images and confirmed by the elongated diffraction spots (Figure 4.12c inset). Previous studies of ScGaN grown in N-rich conditions already suggested a relation between the Sc content and the stacking fault concentrations [64]. However, in this case it is difficult to relate the defect density to the thin film composition due to the different thicknesses of the thin films under study. Particularly interesting is the fact that when the Sc concentration is further increased (Sample E), the defect concentrations drop with an overall improvement of the crystal quality of the thin film. This improvement is confirmed by both HR-TEM images (Figure 4.12d) and the relative diffraction pattern (Figure 4.12d inset). This result is in agreement with the rocking curve results, suggesting that the specific concentration of Sc in Sample E leads to an abrupt improvement of the ScGaN crystal structure.

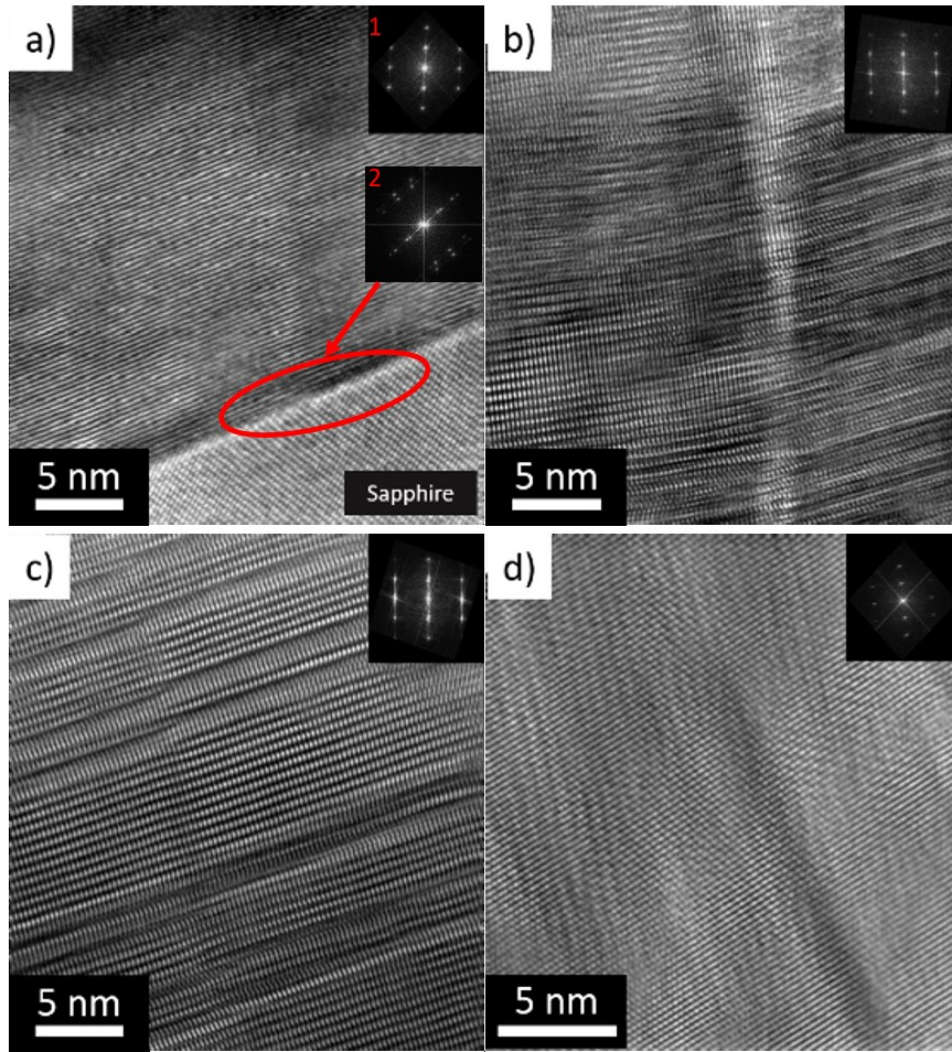


Figure 4. 12 High-resolution TEM images of GaN (a) and $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ with x equal to 0.05 (b), 0.12 (c) and 0.20 (d). The images are taken at the $11\bar{2}0$ zone axis using a 50-cm objective aperture

Since binary ScN is stable in a rock-salt cubic structure, it would be expected that for increasing concentrations of scandium the wurtzite structure of ScGa_{1-x}N distorts towards a wurtzite-like structure leading to higher concentrations of defects. However, in the thin films shown in this work when the concentration of scandium increases the crystal quality improves, while the defect concentration drops. With the help of Dr Giorgio Divitini, HR-STEM was used to further investigate the crystal structure of sample E and the defects present in its structure. The HR-STEM images of ScGa_{1-x}N with highest concentration of Sc are shown in Figure 4.13a and b. First, it is noticed that no contrast related to possible secondary phases is evident, which is consistent with the LR-STEM results (Figure 4.3). This lack of secondary phases suggests that ScGa_{1-x}N grown in e-beam PVD in these conditions is stable in wurtzite structure without undergoing any spinodal decomposition. These conclusions are also consistent with Raman results shown in the following section.

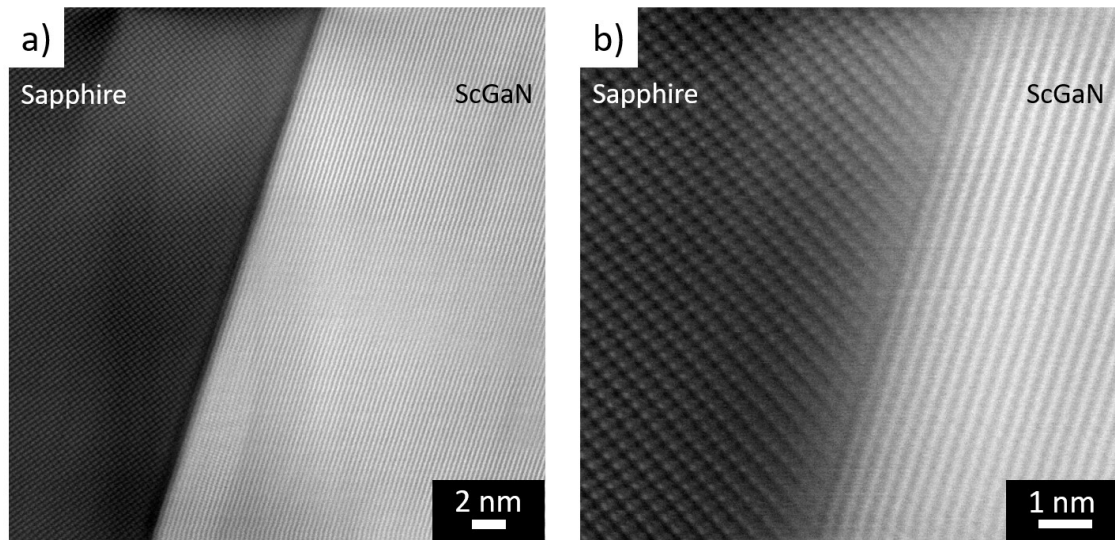


Figure 4. 13 Aberration-corrected HR-STEM images of the interface between sapphire and ScGaN thin film in Sample E.

In addition, even at these magnifications no evidence of stacking faults or dislocations are observed along this zone axis, confirming that for this specific concentration of scandium the crystal-quality level is particularly high. This drastic change in crystal structure is probably a combined result of higher growth rate and good relation between the lattice parameters of ScGaN thin films and the underlying sapphire substrate. It is known that exceptionally slow growth rates favour the adsorption-desorption mechanism of adatoms and the GaN precursor, so that the probabilities to have high concentrations of nanocrystallite misorientations and impurity incorporations increase. Therefore, the higher growth rate of sample E (320 nm/h) may lower the rate of impurity incorporation and the level of misorientations in the structure. In addition, it is possible that for this specific scandium content ScGaN lattice parameter a_{ScGaN} shows a suitable periodicity with a_{sapphire} (i.e. 3 unit cells of sapphire and 4 unit cells of ScGaN have the same length), so that the whole thin film relaxes and the strain in the structure lowers without introducing tredding defects.

4.6 Raman spectroscopy

Raman spectroscopy is used to study the stress level in GaN and ScGaN thin films grown using e-beam PVD. Since only polar structures, such as wurtzite structure, are Raman-active, Raman spectroscopy can be also a useful tool to investigate the crystal quality of the thin films and detect possible non-polar cubic inclusions. Since the rock-salt cubic structure is not polar, in fact, when it is present in the ScGaN thin films it gives rise to broad peaks at 400 and 670 cm^{-1} [157]; therefore, Raman can be used to assess the homogeneity of the wurtzite structure in the ScGaN thin films when the Sc concentration is increased.

Raman spectra of GaN and ScGaN with different Sc concentration are shown in Figure 4.14a and b. While the peaks at 378, 418, 432, 578 and 751 cm^{-1} are related to sapphire, the peak at 568 cm^{-1} is due to the E_2^H mode of GaN and ScGaN thin films. Since the incident laser in the Raman spectrometer is parallel to the c direction, in configuration $z(x,x)z$, the E_2^L and $A_1(\text{LO})$ modes should also be present. However, due to the low thickness of these thin films, it is possible that the intensity of these modes is not strong enough to be detected. As shown in Figure 4.15, when the concentration of Sc increased the peak related to the E_2^H mode shifts at shorter frequencies from 568 cm^{-1} for GaN to 564 cm^{-1} for ScGaN with higher concentration of Sc. The value of GaN thin film is very close to the one reported in literature (568 cm^{-1} [168]) while a red-shift is observed when Sc is introduced in the film. This redshift at shorter frequencies is in agreement with the Raman results of ScGaN grown using MBE [157] and suggests that when the Sc concentration increases the in-plane tensile stress in the thin films increases as well. However, the different thicknesses of these thin films make difficult a comparison of stress levels in these ScGaN structures. In addition, since no fully-relaxed ScGaN thin film is available as reference, it is also possible that this Raman shift is simply due to compositional changes in the ScGaN thin films.

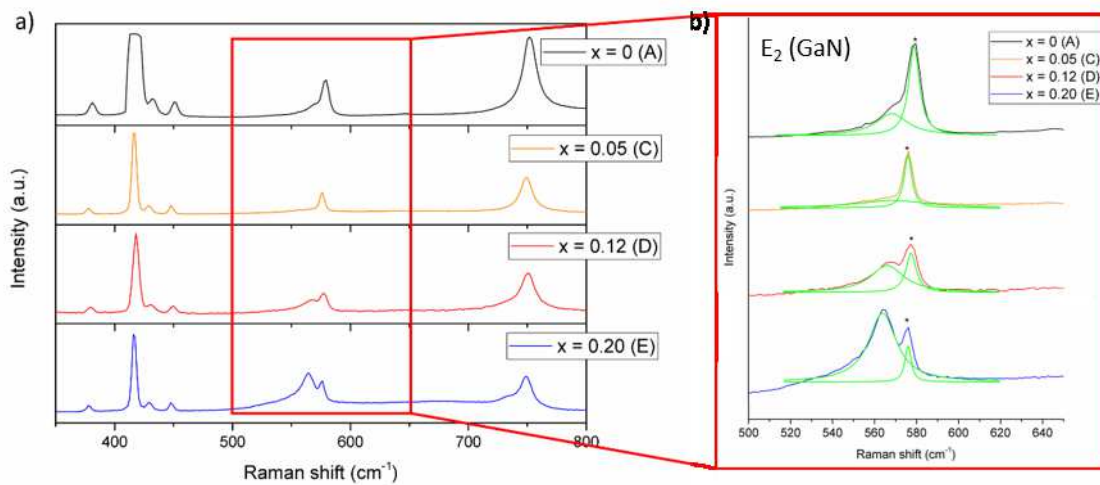


Figure 4. 14 Raman spectra of GaN and ScGaN thin films (a) and zoom-in on GaN-related E_2 peak at 568 cm^{-1} (b). Sapphire peaks are highlighted by the star.

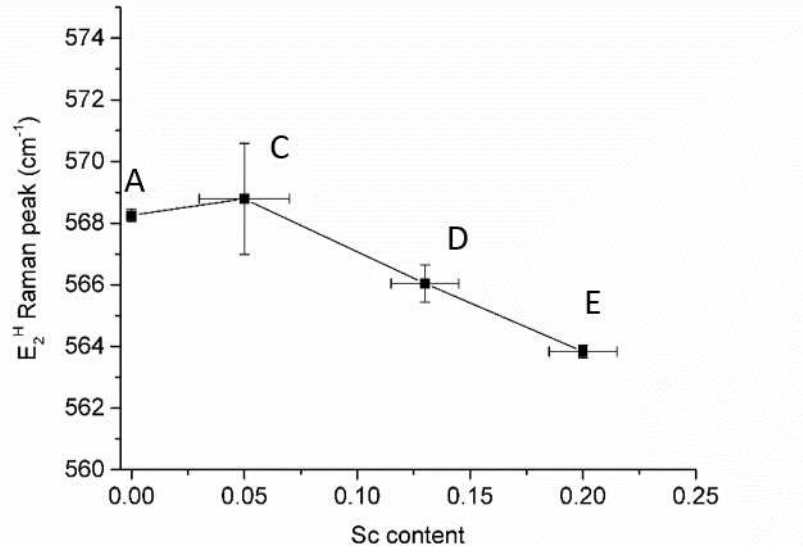


Figure 4. 15 E_2^H positions of GaN and ScGaN calculated from the Raman spectra shown in Figure 4.14.

Finally, in all Raman spectra no broad peaks, usually related to cubic inclusions, are evident. The absence of these broad peaks is in agreement with HR-XRD and TEM results shown in previous sections and conclusively confirms the absence of secondary phases in the ScGaN thin films grown using e-beam PVD.

4.7 Optical characterisation and band gap

The studies of optical properties of III-nitrides and transition metal nitrides (TMNs) are of particular interest for optoelectronic applications such as LED. However, the accurate calculation of the band gap of these materials is also crucial for electrical applications such as high electron mobility transistors (HEMTs). The width of the band gap of the active layer, directly influence the dept of the quantum well generated at the ScGaN/GaN interface and, in turn, the properties of the transistor channel. Therefore, the band gap of GaN and ScGaN thin films grown using e-beam PVD are calculated using both transmittance and reflectance spectra. Moreover, room temperature photoluminescence is also carried out on these thin films.

4.7.1. Transmittance spectroscopy

Transmittance spectroscopy is a powerful non-destructive tool that can be used to assess not only the optical properties of thin films, but also to calculate their band gaps. In this case the sample is illuminated using light with wavelength ranging from 200 to 800 nm or with energy ranging between 1.5 and 6 eV. While the photons with very low energy are transmitted, the photons with equal or larger energy than the band gap of the materials are adsorbed, resulting in a drop of the transmittance curve. Form the position of this drop the band gap of the thin film can be calculated using the Tauc plot [134]. The details of this calculation are discussed in in detail in Chapter 2.

The transmittance spectra of ScGaN thin films under study are shown in Figure 4.16, while calculated Tauc plots are shown in Figure 4.17a. The band gaps of GaN and ScGaN thin films extrapolated from the linear portion of the Tauc curve are plotted in Figure 14.17b.

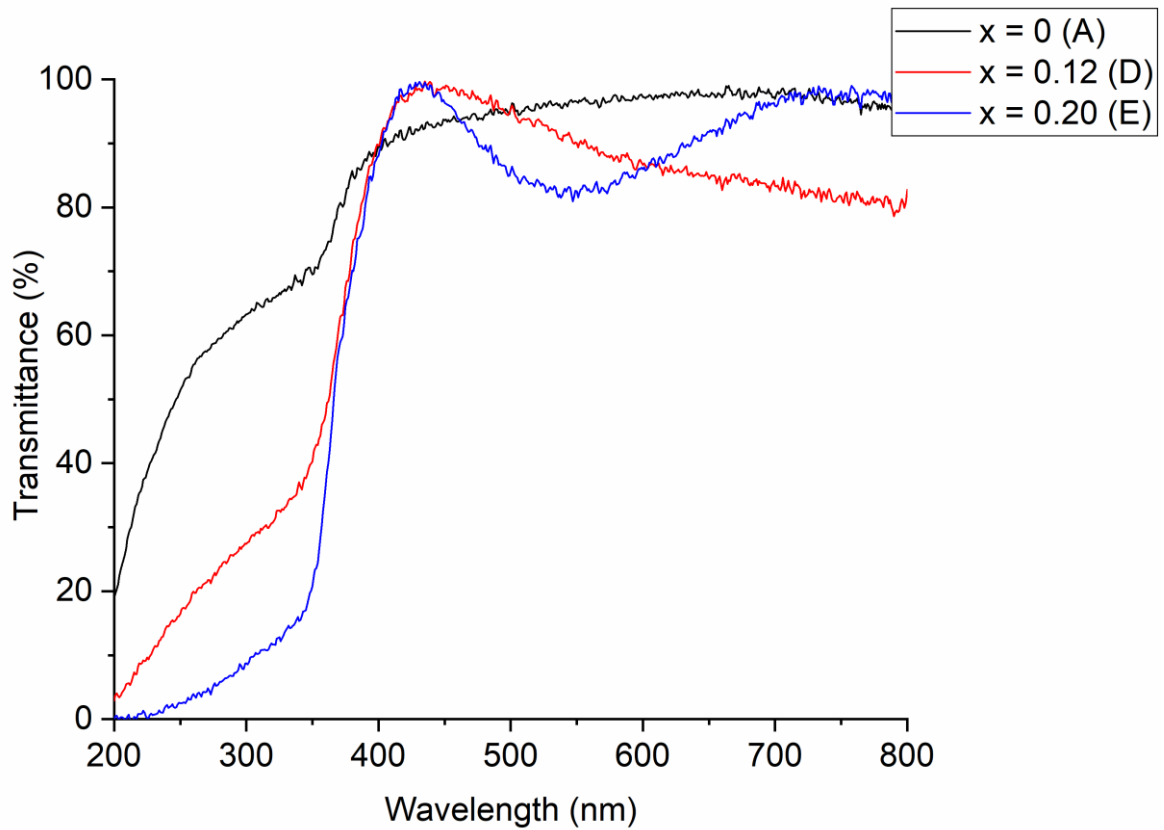


Figure 4. 16 Transmittance spectra of GaN and ScGaN with Sc concentration of 12 and 20 %.

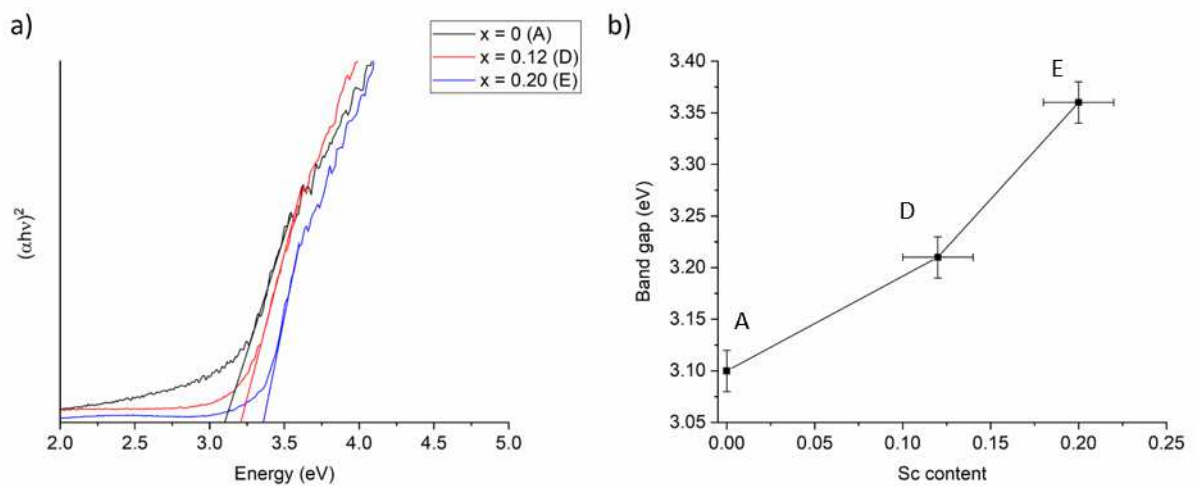


Figure 4. 17 Tauc plot (a) and extrapolated band gap values (b) of samples A, D and E.

From the Tauc plot it is evident that when the Sc concentration in the thin film increases the band gap increases as well and is equal to 3.36 eV for the ScGaN with highest concentration of Sc (Sample E).

This increment in the band gap is consistent with both theoretical calculation and previous ScGa_N experimental studies [21], [66]. It has been observed that the band gap of these thin films is strictly dependent on both defect and impurity concentrations, which are believed to lead to narrower band gaps [64], [67]. For ScGa_N thin films grown using e-beam PVD, the increment of the band gap for higher concentration of Sc is consistent with both a reduction of structural defects and the lack of oxygen impurities, as proven by the TEM and SIMS results respectively.

4.7.2. Reflectance spectroscopy

Reflectance spectroscopy can also be used to calculate the band gap of thin films. In this case an integrating sphere is loaded in the instrument in order to measure the overall and diffuse reflectance. Different methods can be used to calculate the band gap from the diffuse reflectance spectra and most of them are discussed and compared in Ref [135]. However, among them the Kubelka-Munk equations is believed to be the most accurate and reliable method, therefore it has been chosen to calculate the band gaps of the thin films studied in this work. In this case the ratio between the absorption (k) and the scattering (s) indexes is plotted against the energy expressed in eV, and the band gap is obtained by the linear extrapolation of the linear portion of the curve [135].

The reflectance spectra and the curves calculated from the Kubelka-Munk function for GaN and ScGa_N thin films are reported in Figure 4.18 and Figure 4.19a respectively. In addition, the calculated band gaps for different Sc concentrations are plotted in Figure 4.19b.

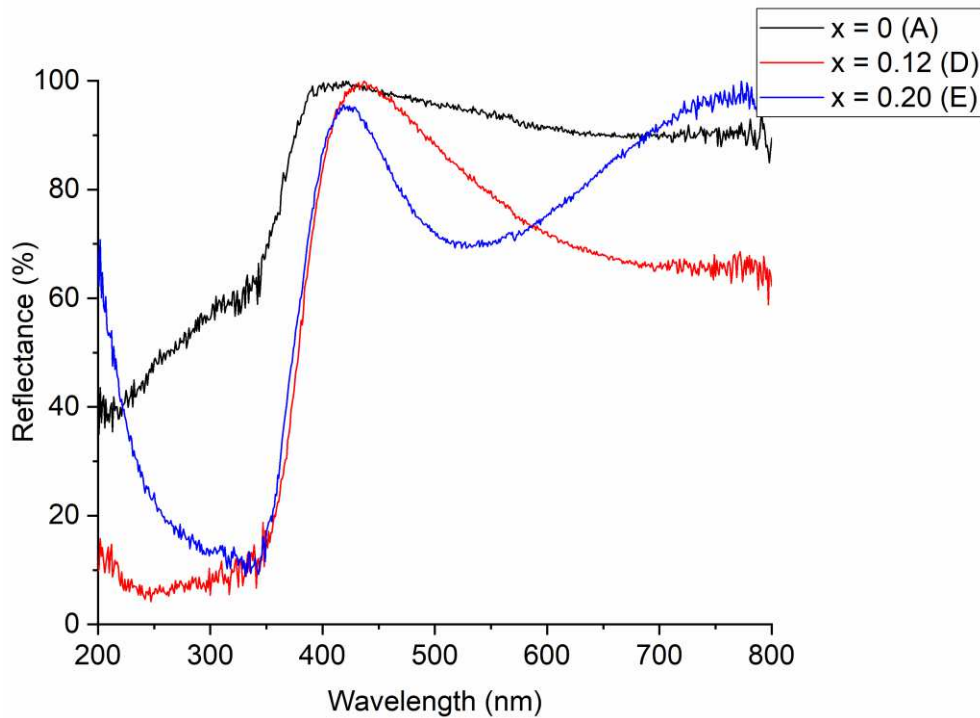


Figure 4. 18 Reflectance spectra of GaN and ScGa_N with 12 and 20 % of Sc.

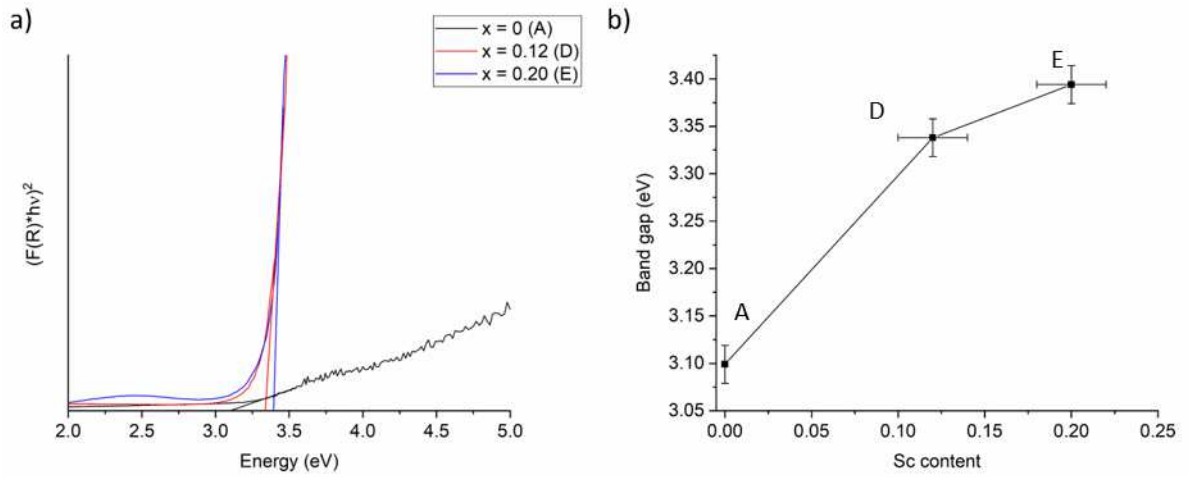


Figure 4. 19 Kubelka-Munk plot (a) and extrapolated band gap values (b) of samples A, D and E.

Once again, a clear trend is evident when the Sc concentration increases in ScGaN thin films up to 3.39 eV for the highest concentration of Sc. Although this trend is consistent with the results obtained using the Tauc plot (Section 4.7.1), it is interesting to notice that the absolute values of the calculated band gaps change when the extrapolation method changes. The band gap values obtained using the two different methods are compared in Table 4.4. This variation in absolute values is possibly related to different accuracy of the extrapolation method: while the Tauc plot takes into consideration the thickness of the thin films, in the Kubelka-Munk function the thin films are assumed to be thick enough so that the sample holder and the thickness of the sample have no influence on the analysis [136]. On the other hand, when transmittance spectroscopy is used, it is assumed that all the not transmitted light is absorbed, while some portion of it might be reflected. In addition, the band gap values obtained using the reflectance spectra are closed to the ones reported in literature, therefore it appears that the band gap values obtained using Kubelka-Munk function might be the more reliable ones.

Sample	Sc content	Tauc plot (eV)	K-M (eV)
A	0	3.10 ± 0.02	3.10 ± 0.02
D	0.12 ± 0.02	3.21 ± 0.02	3.34 ± 0.02
E	0.20 ± 0.02	3.36 ± 0.02	3.39 ± 0.02

Table 4. 4 Band gap values of Samples A, D and E obtained using Absorption spectra, Tauc Plot and Kubelka-Munk function.

4.8 Photoluminescence spectroscopy

To characterize further the optical properties of these thin films, room-temperature photoluminescence (PL) analysis was performed. PL spectra of semiconductor thin films, such as GaN, generally show a sharp, intense peak at about 365 nm and a broad peak at lower energies. The intensities of these peaks

are generally used, not only to study the optical properties of the thin film under study, but also to directly measure the band gap and evaluate the crystal quality of the structure. In PL spectra of thin films, such as GaN a sharp narrow peak, the near-band-edge (NBE) peak, lies at about 3.4 eV and corresponds to the energy of the band gap of the thin film. In addition, a broad peak at lower energy is usually observed, called yellow luminescence (YL). This second peak is believed to be related to the defects of the film, such as structural defects and vacancies; therefore, from its intensity a qualitative estimation of the structural quality of the thin film can be done.

PL spectra of GaN and ScGaN thin films under study are shown in Figure 4.20. The expected peak at 360 nm is not evident in any of the ScGaN thin films, while a weak shoulder is present in GaN curve (sample A). In addition, a broad peak around 450 nm is observed in all samples. This broad peak could be due to the presence of defects, such as stacking faults, or impurities within the film, however no trend is evident when the scandium content is increased. Such that, it is likely that the low growth rates have a major role in the photoluminescence properties, rather than the increasing content of the scandium.

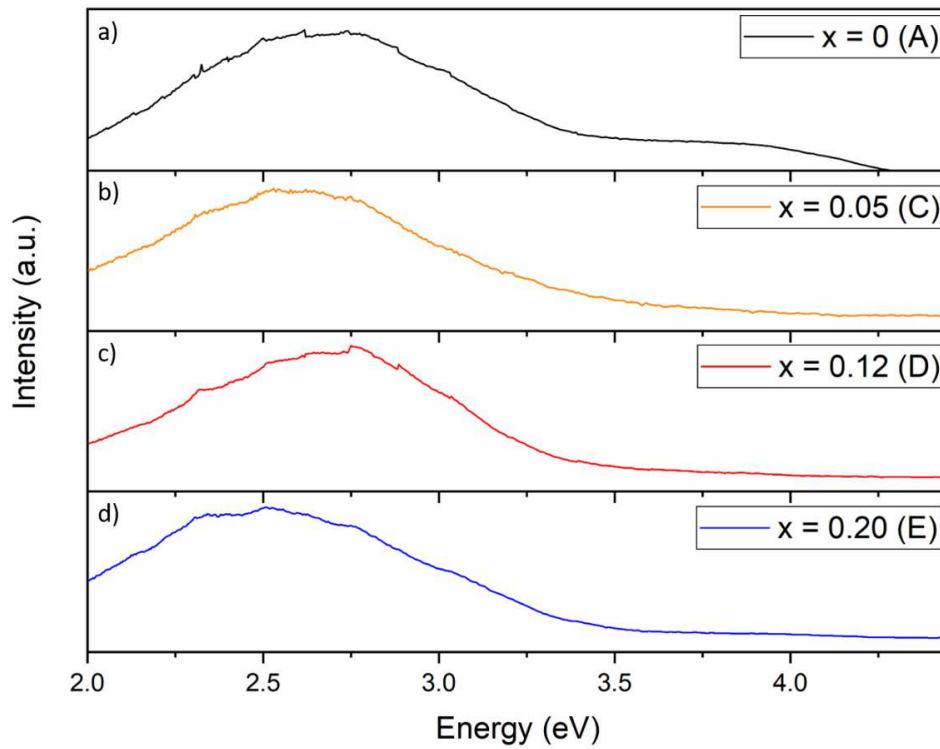


Figure 4. 20 Room temperature photoluminescence spectra for GaN (a) and ScGaN thin films with Sc of 5 % (b), 12 % (c) and 20 % (d).

4.9 Conclusions

Epitaxial ScGaN thin films with different concentrations of Sc have been successfully grown directly on sapphire using e-beam PVD. The growth rate was found to be strictly dependent on the concentration of Sc present in chamber and quickly increases for higher Sc concentrations. This increase is probably

related to the catalytic reaction between Sc and molecular N_2 , which leads to higher concentrations of reactive nitrogen during the growth. This increase of nitrogen makes difficult to predict if the growth takes place in metal- or N-rich conditions; AFM analysis and results reported in literature suggest that these ScGaN thin films are grown in N-rich or Ga-poor Metal-rich conditions. However, the exact regime is difficult to estimate. In addition, a relation between nanocrystallite size and Sc concentration is also observed, which might suggest that higher concentration of Sc results in higher crystal quality of the structure. This relation is also confirmed by the HR-XRD and TEM results, which show an abrupt improvement of the crystal structure for the thin film with highest concentration of Sc. This improvement is believed to be related to a favourable relation between the lattice parameter of ScGaN with that specific concentration of Sc and the underlying sapphire substrate. This relation might lead to a reduction of the stress in the thin film which results in a much lower concentration of stress- and relaxation-defects in the structure. This reduction of defects for this ScGaN thin film was also confirmed using HR-STEM analysis. Moreover, no cubic inclusions were found in any of the ScGaN thin films, as confirmed by both STEM and Raman results.

The optical properties of these thin films have been studied and the band gaps calculated using both transmittance and reflectance spectra. When the Sc concentration increases, an increase of the band gap is observed in both cases. This increase is consistent with the low concentration of defects in the ScGaN structure and with the absence of impurities, such as oxygen, as observed in SIMS results.

Chapter 5

Characterisation of (Fe,Ga)N

5.1 Introduction

In this chapter the study of GaN thin films doped with increasing concentration of iron and grown using e-beam PVD is carried out. It is known that when small concentrations of Fe substitute Ga in the wurtzite structure, Fe introduces acceptor-like states within the band gap that compensate the GaN conductivity and lead to semi-insulating behaviour [87]. Because of this semi-insulating behaviour, Fe-doped GaN has recently attracted great interest for electrical devices such as HEMTs [80], [81], [87]: if a Fe-doped GaN layer is introduced between GaN buffer-layer and sapphire in the HEMT structure, the unwanted background current affecting the buffer-layer is partially compensated and the insulation of the final HEMT improved. However, the solubility of transition metals such as Fe and Mn in GaN is extremely low and ranges around 1 and 6 % for (Fe,Ga)N and MnGa₂N, respectively [79]. Therefore, the growth of homogenous FeGa₂N (or MnGa₂N) without any transition metal-rich precipitates is still relatively challenging. When the concentration of the transition metal is higher than the solubility limit, in fact, spherical transition-metal-rich nanocrystals have been observed [72], [79]. Moreover, Bonanni and collaborators [88] reported that when these nanocrystals are present in the structure, an increment

of carrier concentration was observed with a consequent reduction of the semi-insulating behaviour of the thin film [88].

The structural and electrical properties of Fe-based GaN thin films grown directly on sapphire using e-beam physical vapour deposition (PVD) are discussed in this chapter. In addition, the dependence of these properties on the concentration of iron and on the homogeneity of the crystal structure is also investigated.

5.2 Determination of Fe concentration and structure homogeneity

The solubility of iron and other transition metals (TMs) in wurtzite GaN is known to be very low and around 1 – 6 %, depending on the transition metal used. This low solubility is generally related to the presence of unpaired electrons in the *d*-orbitals of the transition metal that destabilise the electronic structure of the TM-based material. In the case of FeGaN, the maximum solubility of Fe is believed to lie between 0.4 and 1 %, depending on the growth conditions and, for Fe concentration higher than these values, spinodal decomposition and Fe-rich nanocrystals are observed [72]. The presence of these Fe-rich nanocrystals not only lowers the crystal quality of the Fe-doped GaN structure, but also influences the electrical and magnetic properties of the material [88]. Further details regarding these Fe-rich nanocrystals are reported in Chapter 1.

Because of the low solubility of iron in GaN matrix and the influence of the Fe-rich nanocrystals on the structural properties of (Fe,Ga)N, the concentration of Fe and homogeneity of the structure must be accurately assessed using appropriate techniques. Initially the quality of the (Fe,Ga)N structure was assessed using HR-XRD technique, and the lack of Fe-related peaks was considered sufficient proof of the absence of any Fe-rich accumulations or inhomogeneity of the structure. However, this technique was found to be not reliable, leading to an overestimation of Fe solubility in GaN structure [79]. Microstructure characterisation techniques, such as energy dispersive X-ray spectroscopy (EDX) and scanning-TEM (STEM), are now considered essential tools to assess the homogeneity of Fe-doped GaN structure and calculate the concentration of Fe in the thin film. Therefore, in this work the iron concentration and homogeneous distribution in (Fe,Ga)N thin films grown using e-beam PVD were investigated using TEM-EDX and STEM.

In Figure 5.1 the STEM images, the EDX maps and the EDX spectra observed for (Fe,Ga)N, grown using increasing Fe e-beam current, are reported. From these STEM images it can be seen that the (Fe,Ga)N thin film grown using Fe e-beam as low as 20 mA (Sample B) has homogenous structure throughout the film, while (Fe,Ga)N grown using 56 mA as Fe e-beam current (Sample C) shows darker regions near the surface (Figure 5.1e). These darker regions can be due to the presence of Fe-rich accumulations or simply to the presence of holes in the near-surface area of the thin film. Therefore,

EDX maps were used to investigate the origin of these darker regions and to calculate the concentration of iron in the thin films under study. From the EDX results of Sample B, the concentration of Fe present in the structure is calculated to be $0.8 \pm 0.1 \%$ while Ga is $99.2 \pm 0.01 \%$ (Figure 5.1d). This concentration of Fe is lower than the solubility limit ($0.4 - 1 \%$) and therefore, homogenous crystal structure is expected in this thin film. As expected, the EDX map of Sample B (Figure 5.1 c) shows homogenous distribution of iron in the structure without any visible accumulation or nanocrystal. The concentration of Fe in Sample C, on the other hand, is calculated to be $4.6 \pm 0.2 \%$ (Figure 5.1h), which is well above the solubility limit of Fe in GaN material. In agreement with the Fe solubility reported in literature, Fe-rich regions can be observed in EDX maps collected for this sample (Figure 5.1f and g).

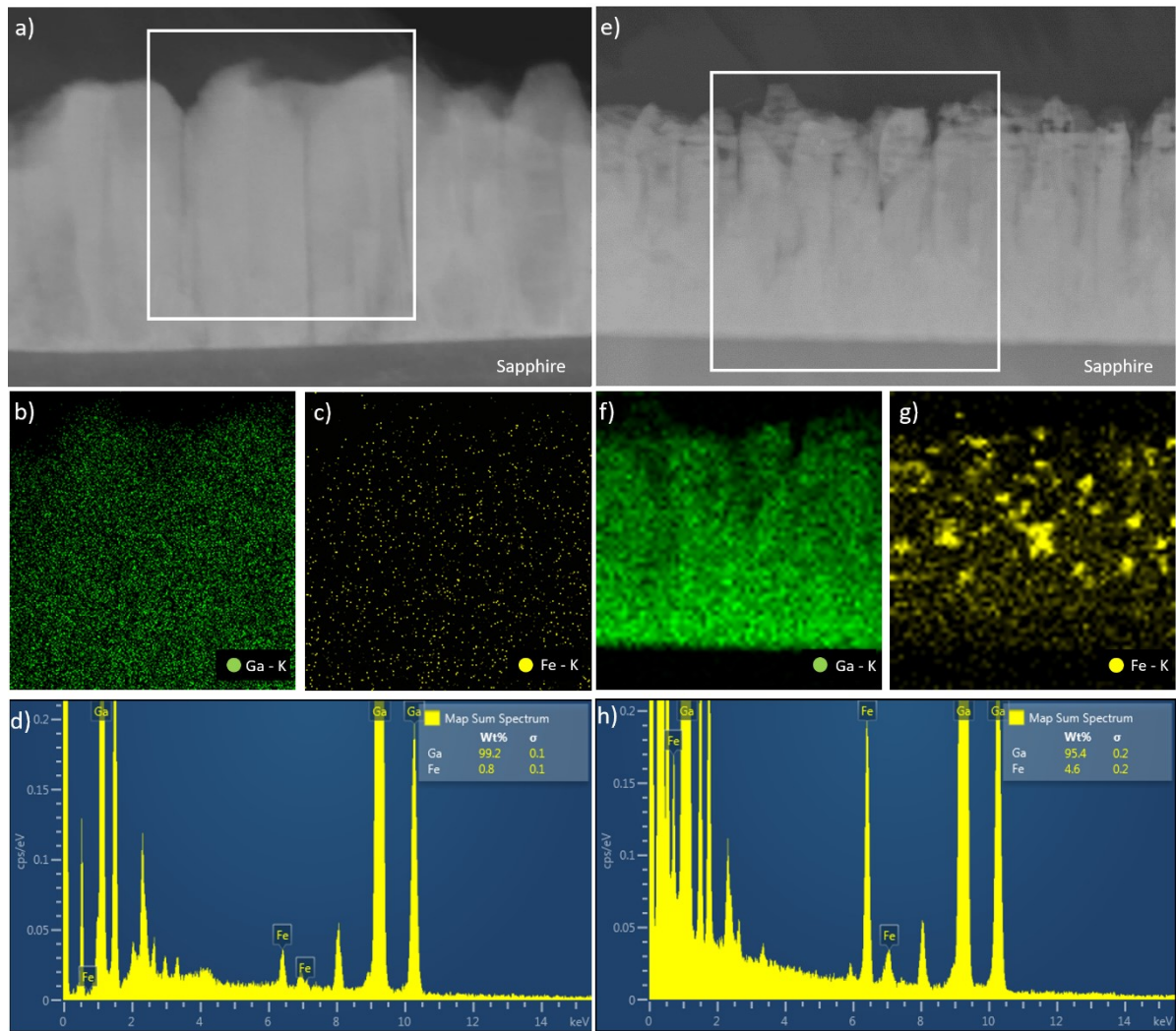


Figure 5. 1 STEM images and EDX maps of Fe-doped GaN grown using Fe e-beam current 20 (a-c) and 56 mA (d-g). The relative mass spectra and Ga and Fe concentration are reported for both Fe-doped GaN grown using lower (d) and higher (h) Fe e-beam current.

In addition, some correspondence between Fe-rich and Ga-poor areas can be observed in Figure 5.1f and g; however, this observation is not reliable enough and further investigation was carried out using EDX maps at high magnifications, illustrated in Figure 5.2. Since the region scanned is very small, the

intensities of the peaks are much lower than those observed in Figure 5.1; nevertheless, a clear Fe-rich – Ga-poor correspondence can be observed in Figure 5.2c and d. These nanocrystals have already been observed in Fe-doped GaN with Fe concentration higher than the solubility limit [72], [88], [90]. Bonanni and co-workers [169] have suggested that when the concentration of Fe in GaN matrix is higher than the limit, a spinodal decomposition takes place driven by the magnetic attraction of the transition metal ions dispersed in the matrix [169]. This decomposition then leads to Fe-rich and Fe-poor regions in the crystal structure, in agreement with the EDX maps shown in Figure 5.2. Similar results have been observed not only in (Fe,Ga)N grown using different growth techniques, but also in other transition metal-doped GaN such as MnGaN and MnGaAs, suggesting a general trend for GaN doped with d-transition metals.

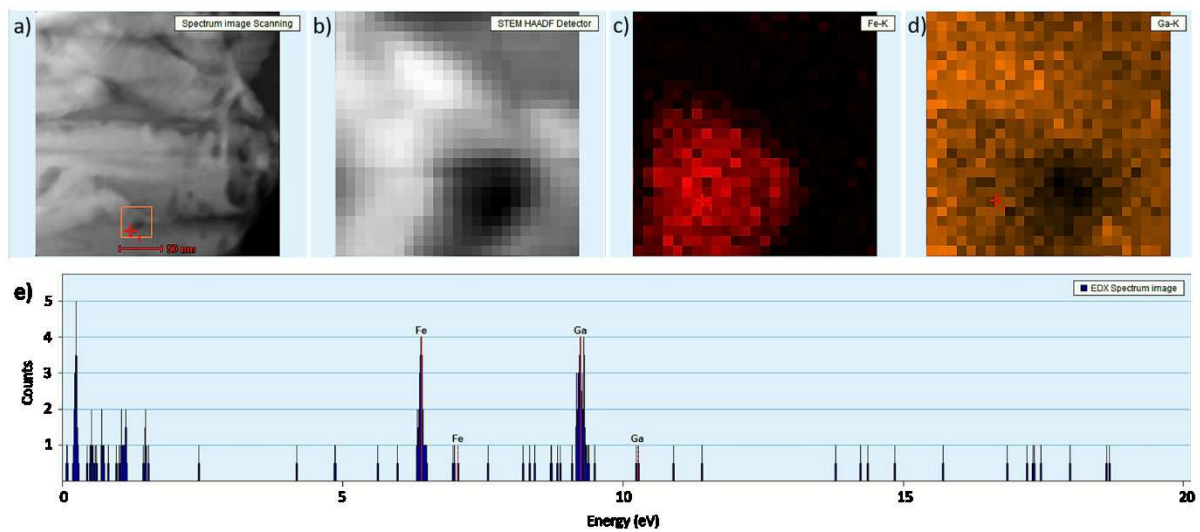


Figure 5. 2 High-resolution STEM images (a-b) and EDX maps (c-d) of a nanocrystal observed in Sample C. The relative EDX spectrum is shown in e.

The presence of these regions is believed to influence the magnetic and electrical properties of the thin films; therefore, further investigation of the nature and structure of these nanocrystals has been carried out and will be discussed later in this chapter.

5.3 Surface morphology

The morphology of unintentionally doped (UID) GaN and Fe-doped GaN with increasing concentration of iron has been investigated using atomic force microscopy (AFM) techniques. In Figure 5.3 the 5 x 5 and 2 x 2 μm^2 topography images of the thin films under study are shown. From Figure 5.3 a and b it is evident that the surface of undoped GaN (Sample A) is covered of droplets of unreacted Ga, while the surface beneath them appears to be very smooth. This morphology is typical of GaN grown under Ga-droplet regime in which the III/V ratio is very high [145]. If the concentration of Ga is much higher than the concentration of N, in fact, Ga adatoms tend to form Ga-rich liquid bilayers in

which Ga adatoms can diffuse until a suitable site is reached. The presence of this bilayer improves the morphological quality of GaN thin films leading to a step-flow 2D growth mechanism [105]. If the AFM images of Sample A are compared with the AFM results of GaN grown under N-rich conditions shown in Chapter 3, in fact, a clear improvement can be observed when GaN is grown under Ga-rich conditions, as expected from literature [145].

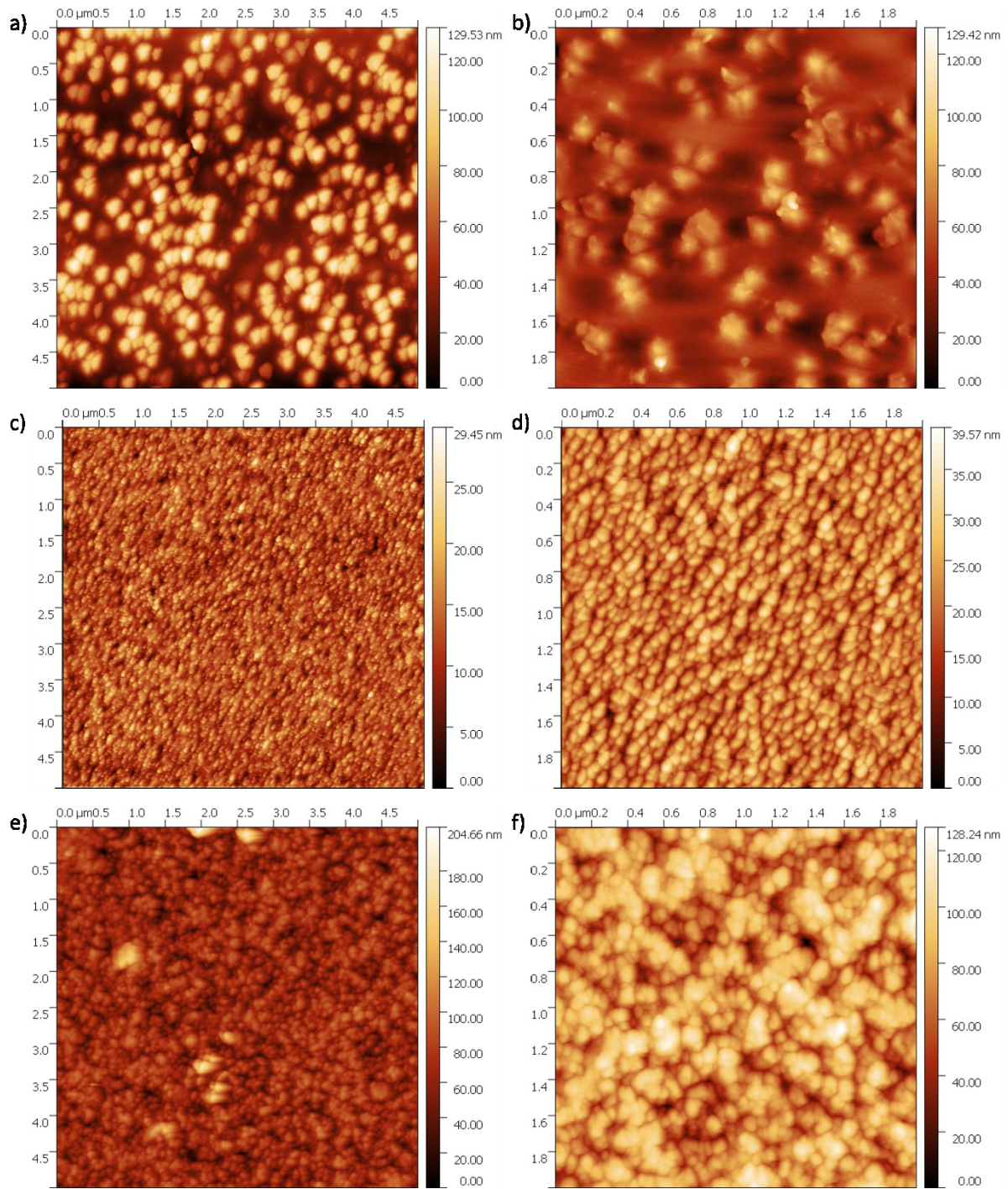


Figure 5. 3x5 μm² and 2x2 μm² AFM height images of UID GaN (a-b) and Fe-doped GaN with Fe concentration equal to 0.008 (c-d) and 0.046 (e-f). All the images are processed using parabolic flattening.

When Fe is introduced in the system, the morphology on the thin films completely changes (Figure 5.3 c-f). Both Fe-doped GaN thin films under study (Sample B and C) show a rough compact surface made of small rounded grains. Since all the other growth conditions remain constant, this change of morphology is expected to be caused by the presence of iron near the surface of the substrate during the growth. Similar morphology variation has also been observed in other transition metal (TM) doped GaN grown using different techniques [83], [170]. Haider and collaborators [165] suggested that the growth conditions of TM-doped GaN can be divided in three different regimes, namely N-rich, Ga-poor but Metal-rich and Ga-rich regimes. When the Ga concentration is much higher than the concentrations of the other reactants, Ga adatoms tend to generate a multilayer in which the surface diffusion of the TM adatoms is much easier than the bulk diffusion. Therefore, under these conditions the transition metal is segregated on the surface and the morphology of TM-doped GaN is comparable to that of binary GaN grown under Ga-rich conditions. When the TM/Ga ratio is increased, the growth takes place in Ga-poor Metal-rich regime. Under these conditions the concentration of TM adatoms is too high to generate a Ga liquid bilayer and the TM tend to adsorb on the surface of the growing thin film. Because of the presence of TM on the surface, the diffusion length of Ga adatoms before reacting is largely reduced, leading to rougher surfaces. However, the roughness of thin films grown in this intermediate regime is found to be lower than in thin films grown in N-rich conditions. This observation suggests that, although the presence of TM reduces the diffusion length of Ga adatoms, it also prevents the accumulation of nitrogen adatoms on the surface leading to intermediate roughness levels [165]. According to this model the Fe-doped GaN thin films under study are grown in Ga-poor Metal-rich conditions.

It is also interesting to notice that when the Fe concentration is increased from 0.8 % (Sample B) to 4.6 % (Sample C), in addition to the rounded nanograins, agglomerates are also visible (Figure 5.3 e-f) and the roughness RMS increases from 5 nm to 17.6 nm. A possible explanation is that in Sample C the concentration of Fe is much higher than the maximum concentration that can be included in GaN structure, therefore Fe adatoms tend to diffuse on the surface without penetrating in the bulk. This 2D diffusion favours the generation of Fe – Fe bonds and the precipitation of secondary phases [171]. The presence of this secondary phase is also suggested by the dots visible in Figure 5.3e and further confirmed by TEM results discussed in the following section.

5.4 Structural and microstructural characterisation

The semi-insulating properties of Fe-doped GaN thin films have attracted increasing interest for III-nitride-based electrical devices, such as high electron mobility transistors (HEMTs). Because of the presence of donor impurities, usually Si or O, unintentionally doped (UID) GaN always shows *n*-type conductivity that limits the performance of the HEMT device, particularly in high-power, high-frequency applications. To limit this problem and compensate this net conductivity, semi-insulating interlayers, such as Fe- or C-doped GaN, have been proposed [81]. However, since the Fe-doped layer

is grown at the base of the entire device, it is crucial that the introduction of iron in the GaN system does not affect the crystal quality of the final device. For this reason, the structural properties of UID and Fe-doped GaN grown using e-beam PVD have been comprehensively studied using different techniques, such as HR-XRD, HR-TEM and Raman spectroscopy.

In Figure 5.4 the XRD patterns of UID and Fe-doped GaN obtained using $2\theta - \omega$ scans are illustrated; in this case the intensity is shown in logarithmic scale to highlight possible small peaks related to secondary phases. From the peaks at 34° and 73° it is evident that in all thin films the wurtzite structure is present and the growth of epitaxial GaN using e-beam PVD is achieved. It is interesting to notice that when a low concentration of iron is introduced in the GaN structure (Sample B) no additional peaks are visible, suggesting that for this iron concentration the structure is not significantly altered and remains homogeneous. This result is in agreement with the EDX maps reported in Section 5.2, in which the iron distribution appears homogeneous throughout the film. However further investigation of the microstructural properties using HR-TEM is still necessary to confirm the absence of any secondary phase or precipitate in the structure.

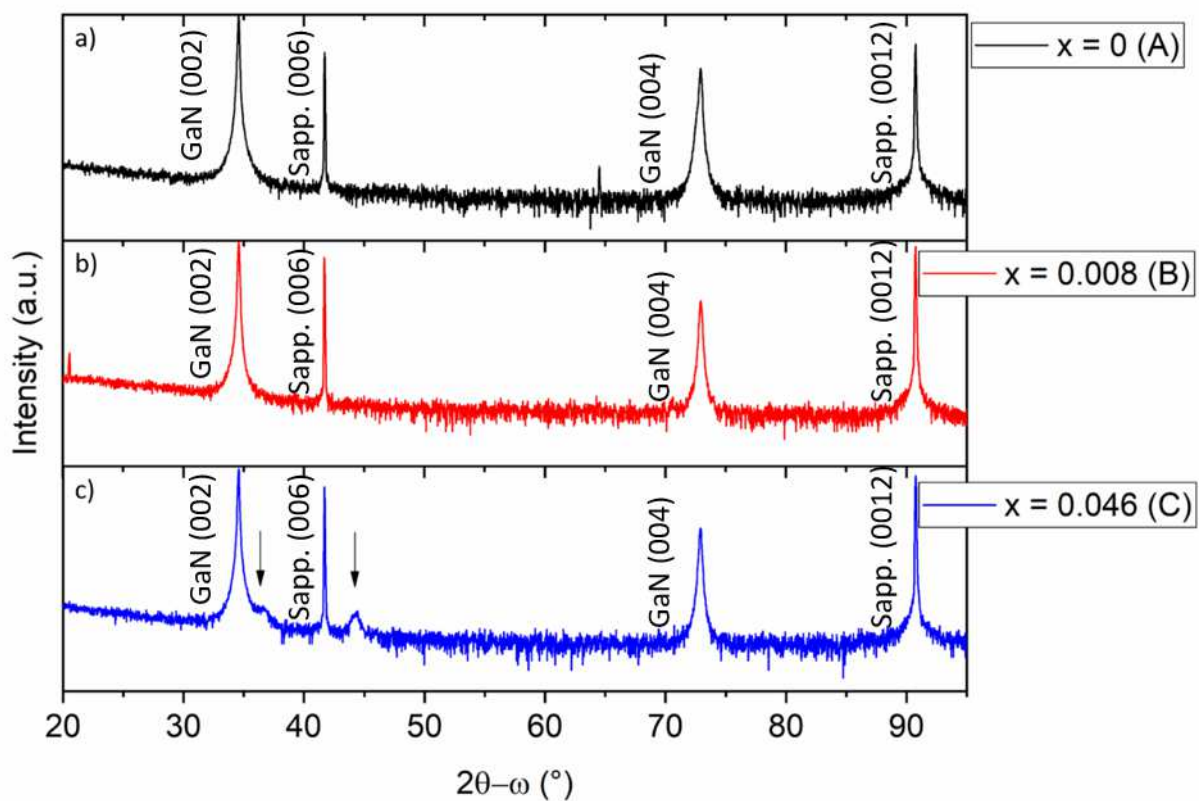


Figure 5. 4 HR-XRD $2\theta-\omega$ scans of UID GaN (a) and Fe-doped GaN with 0.8 % (b) and 4.6 % (c). The peaks related to the secondary phases present in Fe-doped GaN with higher concentration of Fe (c) are highlighted with black arrows.

As expected from EDX results, when the iron concentration is increased to 4.6 %, small additional peaks are observed at 36.2° and 44.3° . These peaks can be attributed respectively to Fe_xN and $\alpha\text{-Fe}$ nanocrystals dispersed in the GaN matrix [172], [173]. To confirm that no other peaks are present in

the patterns, slower scans with improved signal-to-noise ratio were performed between 40 ° and 60 ° on the Fe-doped thin films (Figure 5.5). In this range of 2θ angles no additional peak are observed for GaN doped with lower concentration of Fe (Figure 5.5a); while, a resolved peak at 44.2 ° is observed for higher concentration of Fe (Sample C). This additional peak can be attributed to α -Fe precipitated in the structure. No other peaks attributable to different Fe, Fe_xN or intermetallic Fe_3Ga phases are visible [172], [174]. However, because of the low sensitivity of XRD, the presence of other phases cannot be excluded yet, and further characterisation has been carried out using HR-TEM and diffraction patterns, as discussed later in this section.

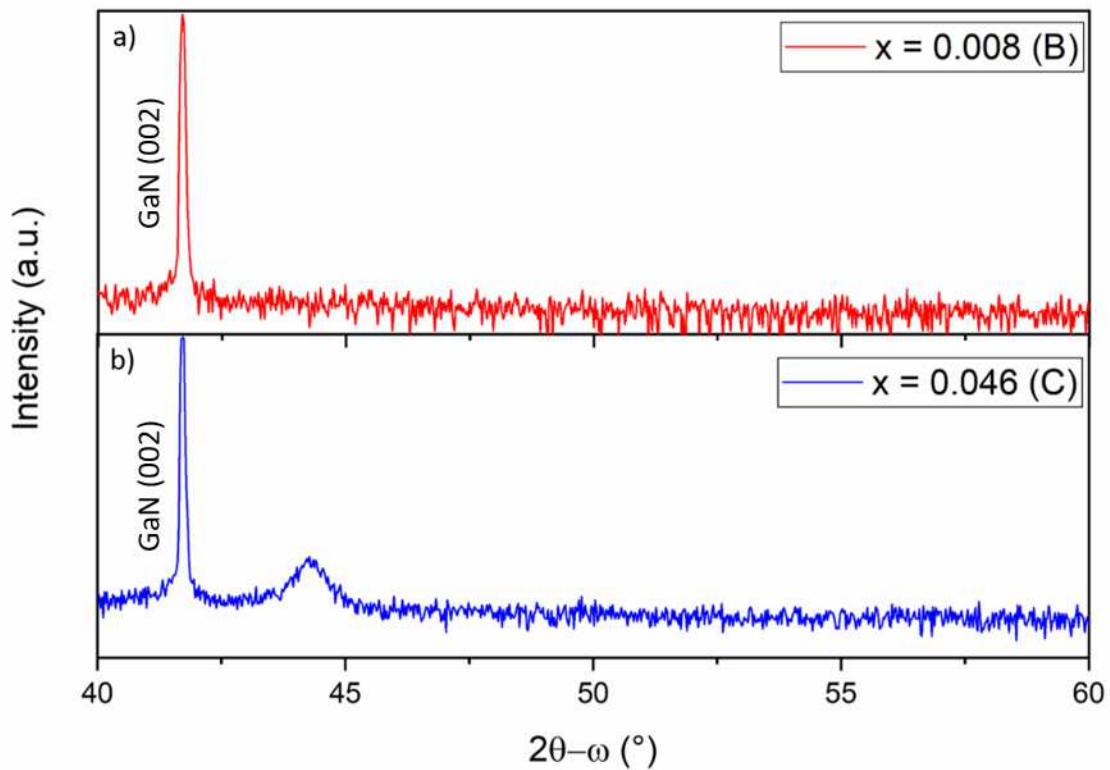


Figure 5. 5 Slower HR-XRD 2θ - ω with increased signal-to-noise ratio between 40 and 60 ° of Fe-doped GaN with Fe concentration equal to 0.8 % (a) and 4.6 % (b).

Using the position of the (002) and (004) peaks of GaN at 34 and 73 °, respectively, the c lattice parameter and the relative strain ε were calculated and reported in Table 5.1. From the calculated c lattice parameter, it is evident that the structure of UID GaN (Sample A) is under relatively large out-of-plane strain. However, when Fe is introduced in the structure (Sample B and C), the c lattice parameter decreases and becomes very close to the ideal value of 5.1851 Å [148]. A possible explanation for this reduction of strain is that, when Fe is introduced, the strain in GaN lattice becomes too high, leading to a relaxation of the structure, possibly via generation of structural defects. This relaxation of Fe-doped structures is also observed in Raman spectra and will be further discussed in the following section.

Name	Fe concentration (%)	(002) GaN position (2 θ °)	c lattice parameter (Å)	Out of plane strain $\left(\frac{c_{exp}-c_{ideal}}{c_{ideal}}\right)$
A	0	34.5445	5.1887 $\pm$ 0.0001	+ 6.9E-04
B	0.8 $\pm$ 0.1	34.5740	5.1844 $\pm$ 0.0001	- 1.4E-04
C	4.6 $\pm$ 0.2	34.5580	5.186767 $\pm$ 0.000004	+ 3.2E-04

Table 5. 1 (002) peak position measured using 2 θ - ω scans, calculated c lattice parameter and out of plane strain of UID and Fe-doped GaN thin films.

To further investigate the crystal quality of the thin films and its dependence on the iron concentration, ω XRD scans (rocking curve) about the (002) peak were performed and reported in Figure 5.6.

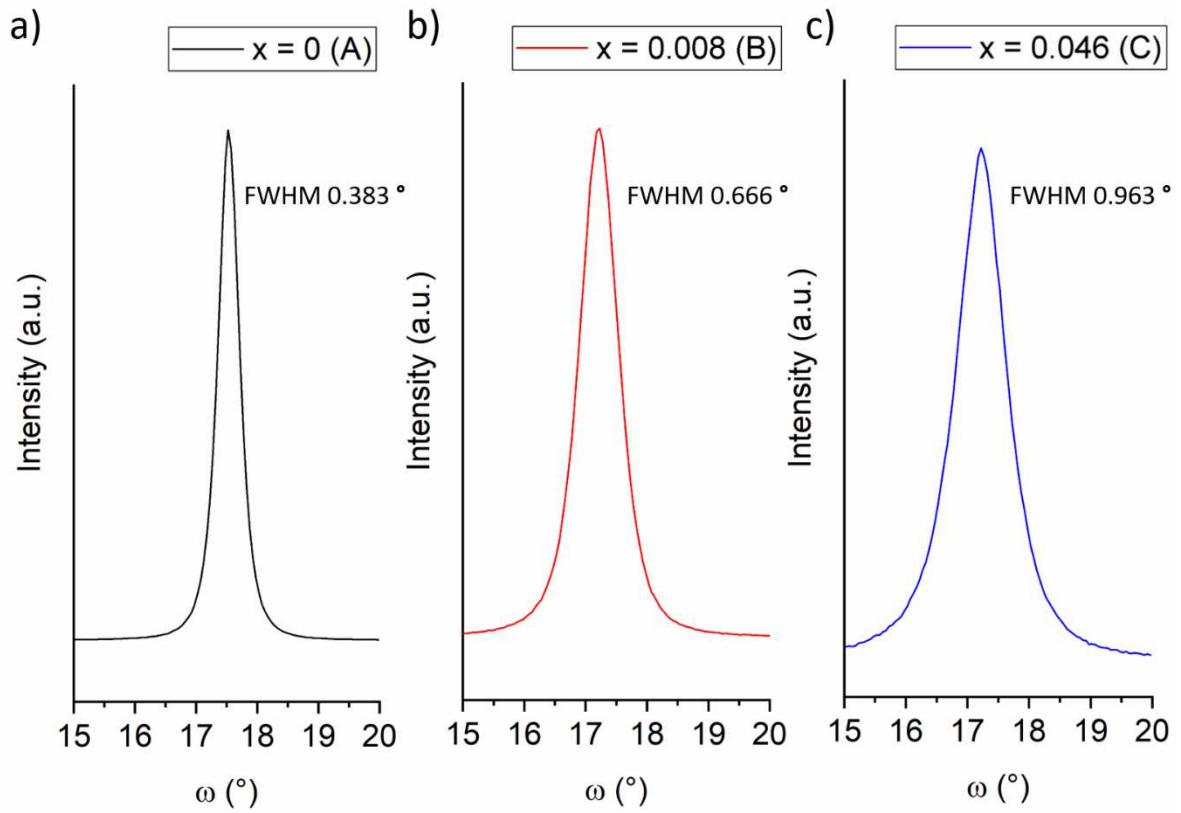


Figure 5. 6 rocking curves obtained from HR-XRD ω scans of UID GaN (a) and Fe-doped GaN with 0.8 % (b) and 4.6 % (c). The full-width-half-maximum (FWHM) values of these curves are also reported.

In agreement with previous results, the full-width-half-maximum (FWHM) values of the curves linearly increase with a factor of about 3 ° when the Fe concentration is increased from 0 to 4.6 %, suggesting that the increasing Fe concentration increasingly reduces the crystal quality. It is also worth noticing that both UID GaN (Sample A) and Fe-doped GaN with lower concentration of Fe (Sample B) show a FWHM narrower than the GaN thin films grown in N-rich conditions discussed in Chapter 3. Although this improvement of crystal quality of UID GaN grown in Ga-rich conditions was expected and largely reported in literature [145], a FWHM as low as 0.67 ° of Sample B was not expected. This result suggests that even if small concentration of Fe introduces defects in the structure, as observed

from TEM results, the crystal quality is still comparable to the one of UID GaN grown in both N- and Ga-rich conditions. As mentioned earlier, this result is of particular interest for HEMT applications in which the introduction of an additional semi-insulating layer cannot lower the quality of the layers above it.

The microstructural properties of these thin films were also studied using bright-field (BF) and high-resolution (HR) TEM and their relative diffraction patterns (DPs). The BF-TEM images of all samples taken along the $[01\bar{1}0]$ zone axis are illustrated in Figure 5.7. In agreement with AFM results, when GaN is doped with iron, columnar structures alternated by deep pyramidal pits become visible (Figure 5.7b and c, black arrow). This change of structure is due to the variation of growth regime from Ga-rich in UID GaN (Figure 5.7a) to Ga-poor Metal-rich regime (Figure 5.7b and c), in which the diffusion length of Ga adatoms is drastically reduced by the presence of Fe atoms on the surface of the growing thin film [165]. In addition, when the Fe concentration is as high as 4.6 %, darker rounded areas, due to the precipitation of Fe-rich second phases, are visible. Moreover, on the top of the columns of this sample a light grey region can be seen: it is possible that this light grey region is related to the presence of unreacted Fe adsorbed on the surface of the thin films, in agreement with AFM images reported in Section 5.3.

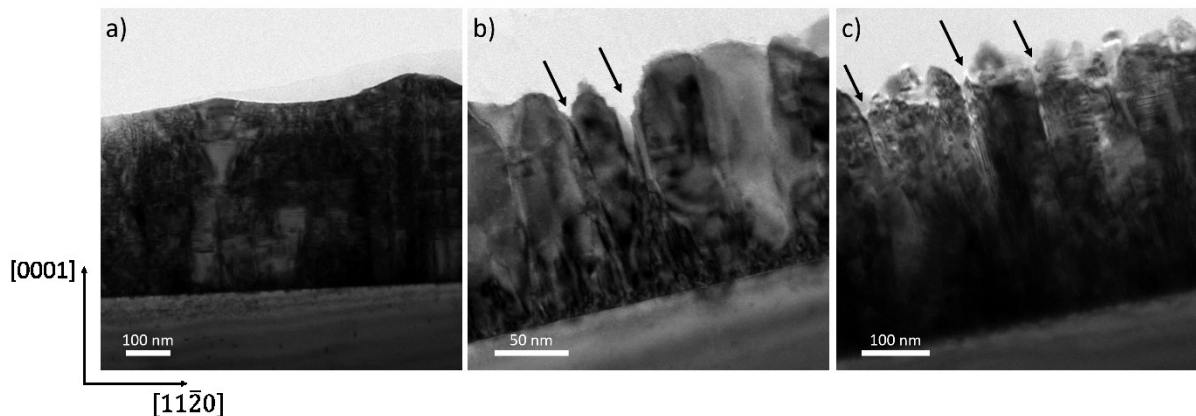


Figure 5. 7 Bright field TEM images of UID GaN (a) and Fe-doped GaN with Fe concentration equal to 0.8 % (b) and 4.6 % (c). The images are taken at the $1\bar{1}00$ zone axis using a 20-cm objective aperture.

HR-TEM and DPs were also used to further investigate the microstructure of undoped and Fe-doped GaN. The HR-TEM images and their relative diffraction patterns of the near-surface, within-the-film and near-interface areas are shown in Figure 5.8. In agreement with rocking curve results, large areas of UID GaN show ordered wurtzite structure with relatively low concentration of defects (Figure 5.8a); however, closer to the interface with sapphire higher concentration of stacking faults (Figure 5.8b) and cubic inclusions (Figure 5.8c) are observed. The presence of these defects near the interface with the substrate can be related to the high strain that the UID GaN undergoes due to the large lattice mismatch with sapphire. When small concentrations of iron are introduced (Sample B), stacking faults normal to the growth direction (Figure 5.8d) and threading dislocations at the column boundaries (Figure 5.8e and

f) appear in the structure. This lower crystal quality for GaN doped with small concentration of Fe is in agreement with AFM and rocking curve results. It is however interesting to notice that for this Fe concentration the structure remains homogenous and few Fe-rich nanocrystals were observed only in one small region of the sample (not shown). Since the presence of these nanocrystals is in contrast with both XRD and EDX results, multiple TEM samples were prepared to assess if this region was representative of the sample. However, no other nanocrystals were observed in the rest of TEM samples of Fe-doped GaN with lower concentration of Fe. Such that, the inhomogeneity of this particular region was attributed to the fluctuation of the local Fe concentration during the growth. The nominal Fe concentration of Sample B (0.8 %), in fact, is very close to the solubility limit reported in literature ($\sim 1\%$); therefore, small local variations of Fe concentration during the growth may lead to local Fe concentrations higher than the average one and, therefore, higher than the solubility limit.

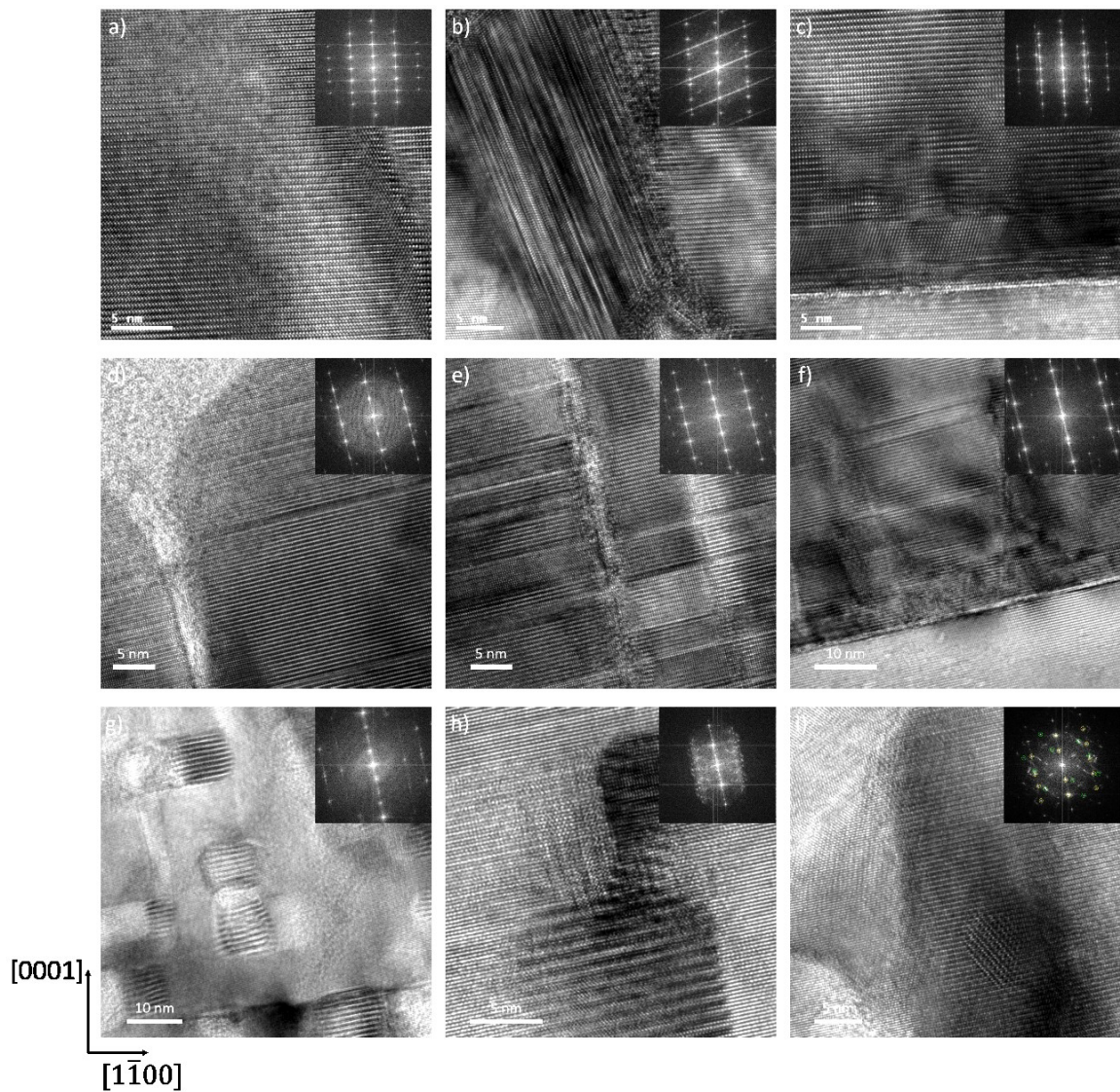


Figure 5. 8 High-resolution TEM images taken at the near-surface, within-the-film and near-interface areas of UID GaN (a-c) and Fe-doped GaN with Fe concentration equal to 0.8 % (d-f) and 4.6 % (g-i). The images are taken at the $11\bar{2}0$ zone axis using a 40-cm objective aperture.

If the Fe concentration is further increased up to 4.6 % (Sample C), the structure becomes largely inhomogeneous and rounded Fe-rich nanocrystals are present near the surface (Figure 5.8g) and within the thin film (Figure 5.8h). The presence of these nanocrystals is in agreement with the EDX and XRD results, as well as the solubility limit reported in literature, which is as low as 1 % [79]. However, it is interesting to notice that no nanocrystals are visible near the interface with the substrate, as shown in Figure 5.7c and 5.8i. This inhomogeneous distribution of nanocrystals along the thin film might be related to the faster diffusion of Fe along the surface rather than down in the bulk. Such that, higher concentrations of Fe are present near the surface while in the lower half of the thin film the local Fe concentration can be below the solubility limit. This surface segregation of Fe during the growth was already observed by Bonanni and co-workers in Fe-doped GaN grown using MOCVD [88], and could justify the large increase of surface roughness observed in AFM when the Fe concentration is increased. However, it is interesting to notice that, even though the Fe adatoms remain segregated on the surface, the crystal quality near the interface of Sample C is largely lower than the crystal quality of the other thin films. As shown in the DP in Figure 5.8i, large misorientation and different growth directions (green and yellow circles) are present in the thin film. These misorientations suggest that the large concentration of Fe adatoms somehow influences the crystal quality of the thin films during the growth, however the mechanism of this interaction is yet not clear.

The nature of the Fe-rich nanocrystals present in Sample C was also identified using selected DPs and HR-TEM images. As observed in EDX results, within the nanocrystal the concentration of Fe is much higher than the rest of the sample, suggesting that these nanocrystals can be a secondary Fe or Fe_xN phase [175] or an intermetallic phase Fe_3Ga [174]. Therefore, the d spacing measured from the diffraction patterns (Figure 5.9) and the XRD additional peak positions (Figure 5.5) were used to identify the nature of these secondary phases. The d spacing of the nanocrystal shown in Figure 5.9a and b is equal to 0.202 nm, which is in agreement with the spacing d_{110} of α -Fe phase [175]. The nanocrystals in Figure 5.9 c and d have a d spacing equal to 0.212 nm, which matches the d spacing d_{121} of ζ - Fe_2N [175]. These results are in good agreement with the additional peaks observed in the 2θ - ω scans of this sample (Figures 5.4c and 5.5b).

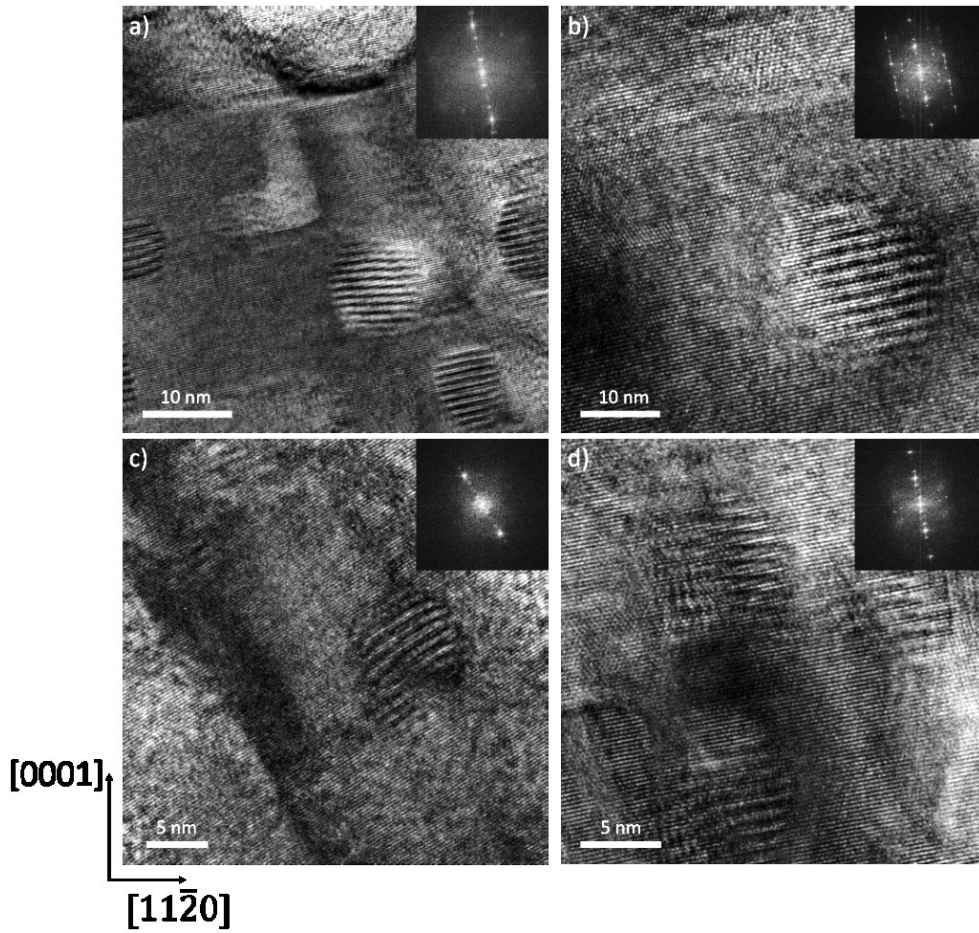


Figure 5. 9 High-resolution TEM images nanocrystals observed in Fe-doped GaN with Fe concentration equal 4.6 %. According to d spacing in this Fe-doped GaN α -Fe (a-b) and ζ -Fe₂N (c-d) are present in the GaN matrix. The images are taken at the $1\bar{1}00$ zone axis using a 40-cm objective aperture.

Finally, from the diffraction patterns of the thin films under study, the c/a ratios were calculated and listed in Table 5.2. From this Table it is evident that UID GaN (Sample A) is under high degree of in-plane compressive stress. The c/a ratio of Sample A, in fact, is much higher than the ideal one (1.6266 Å [148]), due to a reduction of the a parameter, an elongation of the c parameter or a combination of both. As expected from the calculated c lattice parameters, when iron is introduced in the GaN structure the c/a ratio decreases down to 1.856 for Sample C. This relaxation is expected to be related to the higher concentration of defects observed in the Fe-doped samples that reduces the strain in the lattice. Similar results were observed in Raman spectra, as discussed in the following section.

Name	Fe concentration (%)	c/a ratio from DP
A	0	1.8887 ± 0.0002
B	0.8 ± 0.1	1.8715 ± 0.0002
C	4.6 ± 0.2	1.8564 ± 0.0002

Table 5. 2 c/a ratios of UID and Fe-doped GaN thin films calculated from the TEM diffraction patterns.

5.5 Raman spectroscopy

Raman spectroscopy is a non-destructive, contactless technique that can be used to evaluate the crystal quality of the thin film as well as the stress level present in its structure. In this chapter this technique has been used to evaluate the nature and the stress present in UID GaN and the influence of Fe doping on this stress. In Figure 5.10 the Raman spectra of UID GaN (Sample A) and GaN doped with lower (Sample B) and higher (Sample C) concentration of Fe are shown. The peaks visible in these spectra were fitted using Lorentz function and their positions are listed in Table 5.3. As expected from a Raman spectrum obtained using $z(x,x)z$ configuration, the most intense peak related to GaN is the one at 568 cm^{-1} due to the $E_2(\text{high})$ mode; in addition, a second relatively intense peak at about 730 cm^{-1} , due to the $A_1(\text{LO})$ mode, is also visible. The absence of any additional peak in both UID GaN (Figure 5.10a) and GaN doped with lower concentration of Fe (Figure 5.10b) suggests that the crystal quality of the thin films is relatively high and that these low levels of Fe doping do not largely affect the quality of the crystal structure. This result is in agreement with the structural and microstructural results discussed in the previous section and suggests that a level of Fe doping of 0.8 % can be used to obtain semi-insulating GaN layers without lowering too much the quality of the thin film structure.

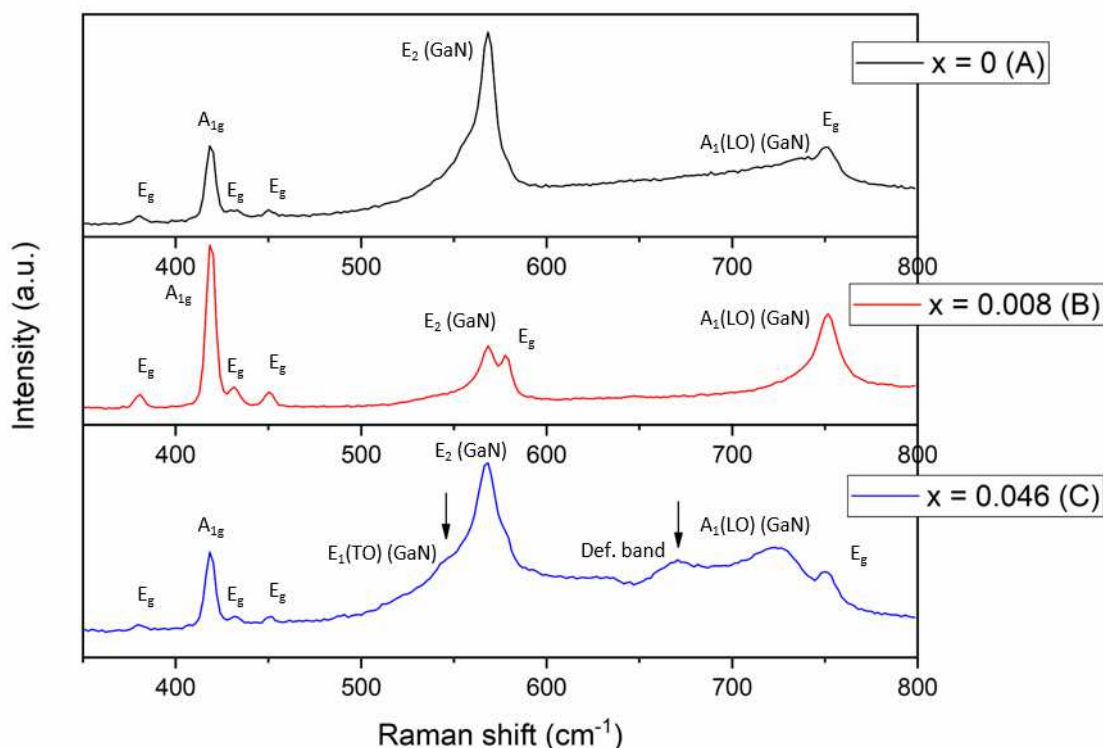


Figure 5. 10 Raman spectra of UID GaN (a) and Fe-doped GaN with Fe concentration 0.8 % (b) and 4.6 % (c).

Name	Sample A	Sample B	Sample C
Fe concentration (%)	0	0. 8 $\pm$ 0.1	4.6 $\pm$ 0.2
E _g – sapphire	381, 435.1, 451.5, 750	3801.2, 431.7, 451, 578.5, 750.1	380.2, 432.3, 451.6, 750.4
A _{1g} – sapphire	419.4	419.5	419.7
E ₁ (TO) – GaN	--	--	551.5
E ₂ (high) – GaN	568.4	568.2	568
Defect band – Fe related	--	--	670.9
A ₁ (LO) - GaN	738	737	724.9

Table 5. 3 Positions of Raman peaks of UID GaN and Fe-doped GaN with Fe concentration equal to 0.8 % and 4.6 % extrapolated from Raman spectra illustrated in Figure 5.10.

If the Fe concentration in doped-GaN is further increased (Sample C), additional peaks at 549.7 and 670.9 cm⁻¹ are observed. The first peak is due to the typical E₁ (TO) mode of GaN; however, this mode is usually not visible in Raman spectra obtained in this configuration. The presence of this peak in Sample C spectrum, and its absence in the spectra of the other thin films, suggests that in this sample the Raman selection rules become more relaxed so that other peaks can be visible in this configuration. The relaxation of the selection rules generally indicates lowering in the crystal quality and high concentration of defects, introduced by the high concentration of Fe in the GaN matrix [172]. The peak at 670.9 cm⁻¹ is also related to high concentration of defects and has already been observed in highly Fe- and Mn-doped GaN grown using metalorganic chemical vapour deposition (MOCVD) [176]. The Raman results of Sample C are also in agreement with the structural and microstructural results discussed earlier, suggesting that, at this high concentration of Fe, disorder and defect concentrations are much higher than in the other thin films under study.

In addition to the structural characterisation, the position of the E₂^H peak in the UID and Fe-doped GaN is used to evaluate the nature and level of stress in the structure. The positions of the E₂^H peak as a function of the Fe doping level are reported in Figure 5.11. From this plot it is evident that all E₂^H peaks are at much higher frequency than the frequency of fully relaxed GaN (568 cm⁻¹ [168]). This blue-shift at higher frequency suggests that all thin films are subject to in-plane compressive stress, which is in agreement with *c/a* lattice parameters obtained from TEM diffraction patterns. In addition, when Fe is introduced in the GaN system the compressive strain is partially relaxed and this relaxation increases when the Fe concentration increases. For Fe-doped GaN with higher concentration of Fe, in fact, the value is very close, to the fully relaxed GaN, suggesting that in this case virtually all strain is released. This red-shift due to the increasing concentration of Fe suggests that the presence of Fe in the structure induces a partial relaxation of the structure. This result is also in agreement with the TEM and XRD results discussed earlier.

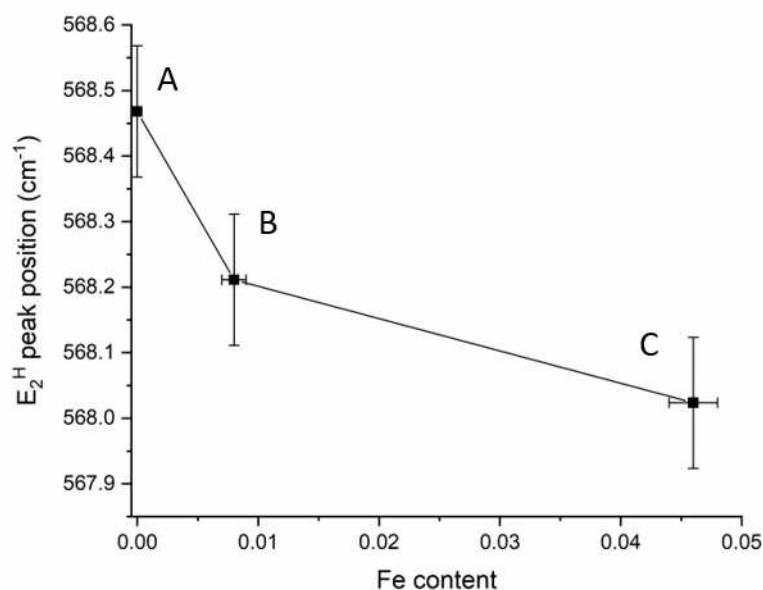


Figure 5. 11 E_2^H peak trend as a function of Fe concentration in UID and Fe-doped GaN thin films extrapolated from Raman spectra.

5.6 Optical characterisation

The optical properties of UID GaN grown in Ga-rich conditions and of Fe-doped GaN have been studied using Transmittance and Photoluminescence (PL) spectroscopy. Although Fe-doped GaN thin films are not usually used directly for their optical properties, these techniques can be used to calculate the band gap of these thin films and study how the presence of Fe in the structure can influence it. The introduction of Fe in GaN system, in fact, is expected to introduce acceptor-like states in the band gap that lie near the bottom of the conduction band. The presence of these localised states generates the semi-insulating properties that are of interest for electrical devices applications, such as high electron mobility transistors (HEMTs) [86]. Therefore, in this chapter the optical properties and the band gaps of UID and Fe-doped GaN are studied. In addition, a strict dependence of the band gaps to the concentration of Fe in the GaN structure is also found and discussed.

5.6.1. Transmittance spectroscopy

Transmittance spectroscopy is a powerful, fast technique that can be easily used to obtain the transmittance and absorbance spectra of a thin film in a non-destructive manner. From these spectra, then, information can be extrapolated, such as band gap, refractive index (n) or absorption coefficient (α). Further detail of the instrument and the Transmittance technique are illustrated in Chapter 2. The transmittance spectra of the sample under study have been obtained using an UV-vis-IR spectrophotometer, loading a support for solid sample and an integral sphere to improve the accuracy of the experiment.

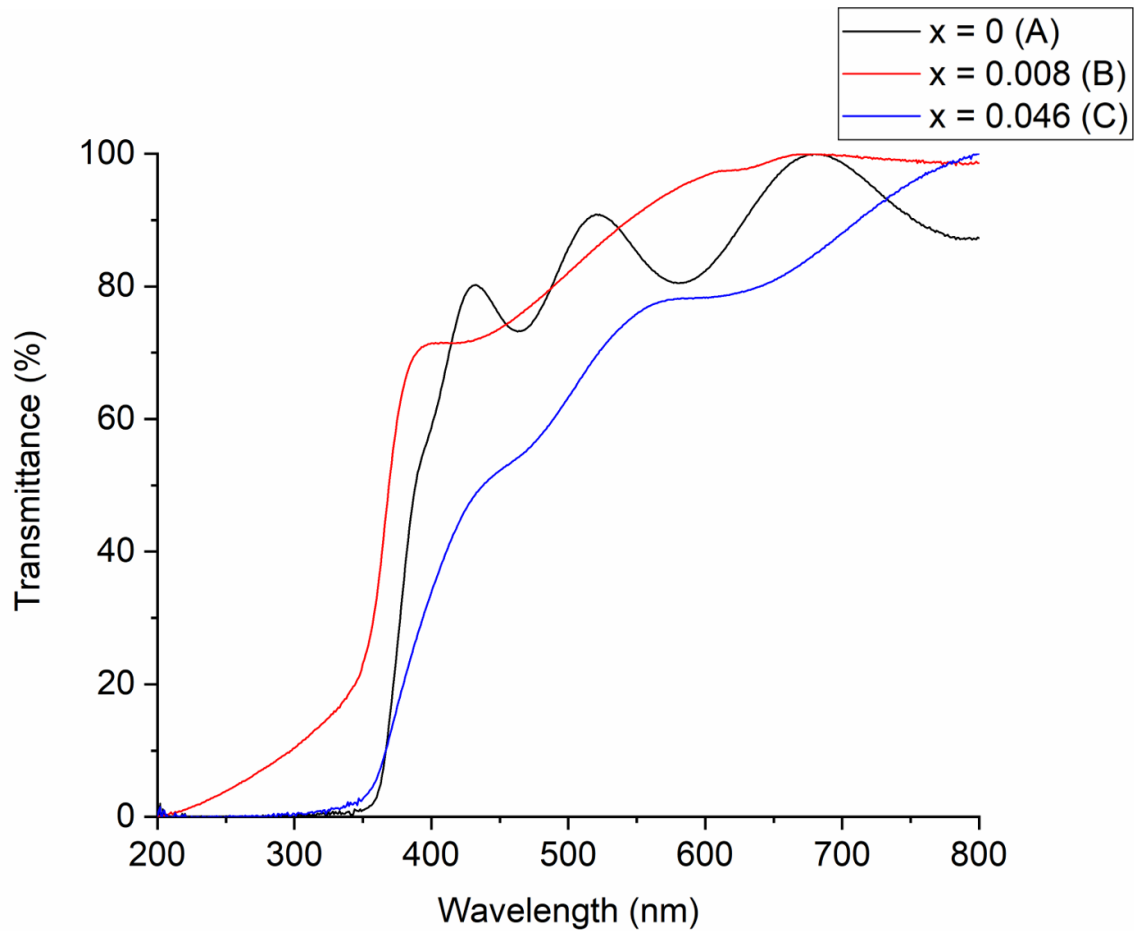


Figure 5.12 Transmittance spectra of UID GaN and Fe-doped GaN thin films in the range between 200 and 800 nm.

From Figure 5.12, it can be seen that the transmittance curve of UID GaN (Sample A) drops at about 365 nm, which is in good agreement with the value reported in literature. When high concentrations of Fe are introduced in the system (Sample C), the transmitted curve drops at much larger wavelength. This drop at larger wavelength suggests that the band gap of Sample C is much narrower than the one of UID GaN (Sample A). The curve of Sample B appears to be relatively different than the other two, with a smaller drop shifted at shorter wavelength. This different shape is expected to be related to the smaller thickness of Sample B (Appendix A) and not to the concentration of Fe in the structure.

In addition, at longer wavelengths interference fringes are visible for all samples; however, the minimum and maximum of the fringes are well defined only for UID GaN, while in Fe-doped the interference structure is nearly destroyed. It is known that these interference fringes are dependent on both the thickness of the thin film and the smoothness of its surface [149]. Therefore, the absence of well-resolved fringes in Sample B might be due to the smaller thickness, and larger wavelength window would be necessary to investigate properly the optical properties of this sample. On the other hand, Sample C has similar thickness to Sample A and the destruction of the interference structure should be mostly related to the lower surface quality of this thin film, as observed in AFM images in Section 5.3. Nonetheless the interference fringes of UID GaN (Sample A) and Fe-doped GaN with higher

concentration of Fe (Sample C) has been used to calculate the optical properties of these thin films. From the transmittance spectra, in fact, the refractive index n and the high-frequency dielectric constant ϵ_∞ can be calculated using the Swanepoel's method [149]. According to Swanepoel's method the refractive index n can be obtained by measuring the refractive index of the substrate s and the transmittance of the maximum (T_M) and minimum (T_m) of the interference fringes and using the following equations.

$$N_1 = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (5.1)$$

$$n = [N_1 + (N_1^2 - s^2)^{\frac{1}{2}}]^{\frac{1}{2}} \quad (5.2)$$

While the high-frequency dielectric constant ϵ_∞ is defined as

$$\epsilon_\infty = n^2 \quad (5.3)$$

The refractive index and high-frequency dielectric constant of Sample A and C are listed in Table 5.4.

Name	Fe concentration (%)	Refractive index (n)	High-frequency dielectric constant (ϵ_∞)
Sample A	0	2.16 ± 0.02	4.67 ± 0.08
Sample C	4.6 ± 0.2	2.7 ± 0.1	7.6 ± 0.5

Table 5. 4 Optical properties of UID and Fe-doped GaN calculated from the interference fringes.

The values calculated for UID GaN are in good agreement with those reported in the literature [153], [177], confirming that UID GaN grown in Ga-rich conditions using e-beam PVD shows relatively high crystal and optical quality. When Fe is introduced in the system the optical constants appear to increase, which seems to be in agreement with the trend reported by Fang and co-worker [178]. Similar increases have also been observed in ScAlN [179] and are expected to be related to a variation of the electronic polarisation due to the presence of the transition metal. However, it must be stated that the uncertainty is directly related to the difference between the maximum and minimum of the fringes and the error on the optical constants of Sample C is relatively high; therefore, the value calculated might not be reliable.

The transmittance spectra illustrated in Figure 5.12 have also been used to calculate the band gap of the thin films under study. As mentioned above, a shift of the band gap to longer wavelength can be clearly observed from the transmittance spectra when the Fe concentration increases from 0 to 4.6 %. However, the band gaps calculated directly from the transmittance spectra are affected by a large error and manipulation of data is necessary to calculate accurately the band gap of the material. A common method used to calculate the band gap of semiconductors from transmittance data is the Tauc plot, in which the absorption coefficient α is multiplied by the energy $h\nu$ and plotted against $h\nu$. In addition, the exponent of $(\alpha h\nu)$ is dependent on the nature of the band gap, as explained in detail in Chapter 2. The Tauc plots of UID and Fe-doped GaN and the trend of the band gap as a function of Fe concentration

are illustrated in Figure 5.13a and b, respectively. As expected, a clear trend is evident when the Fe concentration is increased from 0 to 4.6 % with a large reduction of the band gap. This reduction is well documented in the literature and is expected to be related to the introduction of localised states right below the bottom of the GaN conduction band [86]. These localised states introduced by the Fe atoms act as acceptor-like states and reduce the width of GaN band gap. This reduction of band gap is in agreement with the shift of the near-band-edge peak in PL spectra and the semi-insulating properties of Fe-doped GaN samples discussed in the following sections.

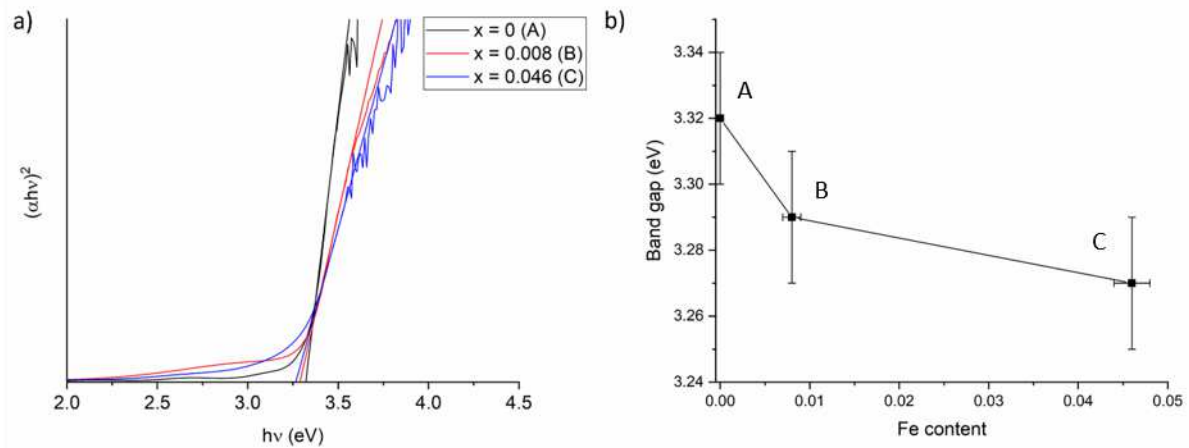


Figure 5. 13 Tauc plot of UID GaN and Fe-doped GaN (a) calculated from the transmittance spectra illustrated in Figure 5.12 and the extrapolated band gap values (b).

It is interesting to notice that the band gap of UID GaN lies at 3.32 eV, which is lower than the value reported in literature (3.4 eV) but much larger than the one observed for UID GaN grown under N-rich conditions discussed in Chapter 3. This larger band gap suggests a reduction of defects and an improvement of structural and optical quality of GaN when grown under Ga-rich conditions, in agreement with structural and AFM results.

5.6.2. Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is another non-destructive technique that can be used to characterise the optical properties of semiconductor thin films. Semiconductor thin films such as GaN generally show an intense peak at the energy of their band gap, called near-band edge (NBE) peak, and a broad band at lower energies, the yellow (YL) luminescence, generated by the structural defects and vacancies present in the structure [180]. Therefore, PL spectra can give information not only about the optical properties but also the electrical and structural properties of thin films. Although PL spectroscopy is widely carried out at room temperature, low-temperature PL experiments are also very useful to study more in detail the band structure of the thin film. If the experiment is carried out at few Kelvins, the thermal noise is reduced, and the luminescence peaks better resolved; such that, in low-

temperature PL experiments additional peaks related to sub-band transitions can usually be observed [86]. Further details about PL technique are reported in Chapter 2.

In this work, room-temperature PL experiments were carried out on UID and Fe-doped GaN thin films grown using e-beam PVD and the resulting spectra are reported in Figure 5.14.

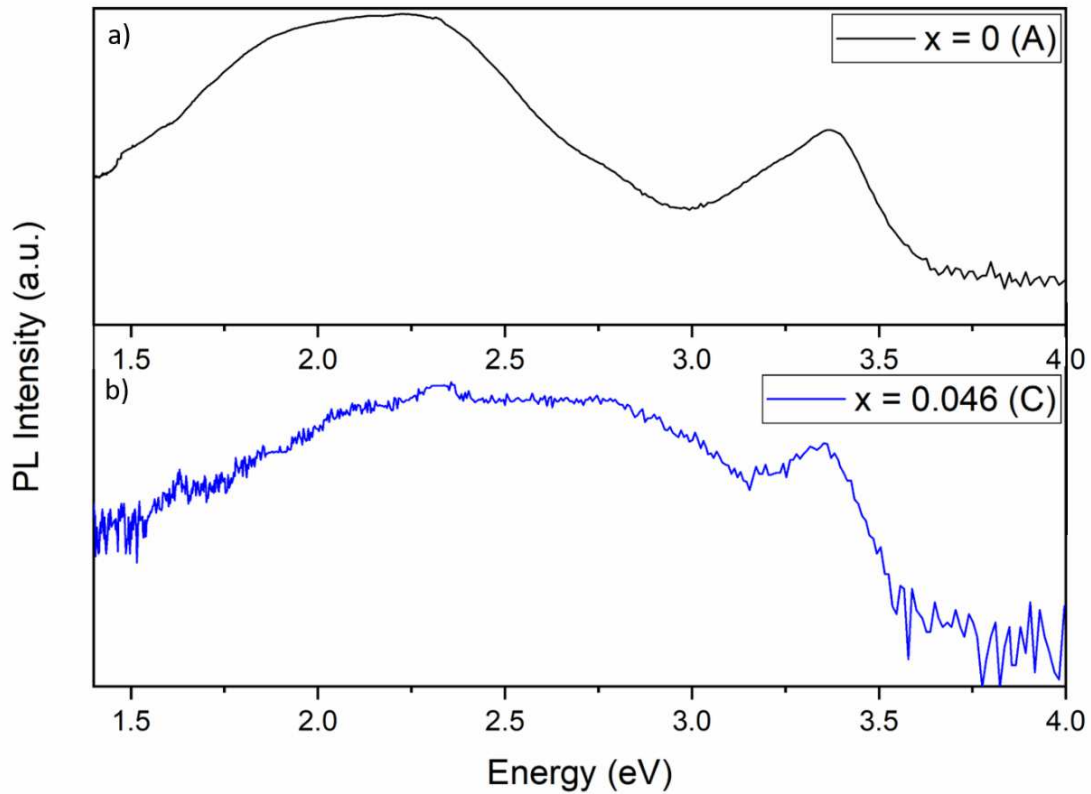


Figure 5. 14 Photoluminescence spectra of UID GaN (a) and Fe-doped GaN with Fe concentration equal to 4.6 % (b).

UID GaN shows a relatively intense peak at 3.37 eV and a broad band at about 2.33 eV. These peaks are typical of GaN thin films and can be identified as near-band-edge (NBE) and yellow luminescence (YL), respectively [180]. As mentioned above, the first gives information about the band gap of the thin film and is in good agreement with the value widely reported in literature (3.4 eV). It is interesting to notice that the band gap value obtained from PL is slightly larger than the one calculated using the Tauc plot (3.32 eV). Since manipulation of transmittance data and extrapolation of the linear portion of the Tauc plot are necessary to calculate the band gap using Transmittance technique, the PL band gap can be considered more reliable, since no manipulation is necessary to obtain the NBE peak. In addition, it is interesting to notice that the YL at 2.33 eV is very intense and even more intense than the NBE. The origin of this peak is still under discussion, however there is a consensus that the intensity of this peak is related to the concentration of defects, such as stacking faults and Ga vacancies [154], [180]. The presence of a relatively high concentration of defects can be understood considering that this thin film is only 400 nm thick and directly grown on a sapphire substrate. Accordingly, the crystal quality of the

thin film is expected to be easily improved, with a consequent reduction of the YL intensity, by employing GaN templates grown using more optimised techniques such as MOCVD.

As shown in Figure 5.14b, when Fe is introduced in the GaN structure the overall PL spectra becomes less intense and noisier. Similar reductions of luminescence have already been observed in Fe-doped GaN grown using hydride vapour phase epitaxy (HVPE) [84] and might be related to the lower carrier concentration present in Fe-doped GaN [181]. Despite the lower intensity, the NBE peak is still visible in the Fe-doped spectrum and shifted at 3.33 eV. This reduction of band gap is in agreement with both literature results and the value calculated using Transmittance spectroscopy (3.27 eV), and is caused by the introduction of Fe-related acceptor-like states lying below the bottom of the conduction band. Because of these acceptor-like states, Fe-doped GaN is expected to show semi-insulating behaviour, as discussed in the following section. It is also interesting to notice that the band gap value of this sample obtained from PL is also larger than the one calculated using Tauc plot. Because of this underestimation of band gap when Tauc plots are used, it might be advisable to use this technique only to obtain the variation of the band gap when the Fe concentration is changed, rather than the absolute values.

In addition to the NBE peak, only another broad peak centred at about 2.5 eV is visible in the PL spectra of Fe-doped GaN (Figure 5.14b), generated by the YL. It is interesting to notice that, compared to UID GaN spectra, the intensity of the YL in Fe-doped GaN is much lower. This suppression might be related to a partial compensation by Fe-doping of donor-like states possibly introduced by Ga vacancies or donor impurities such as Si [84], [181]. Another possibility is that the reduction of the YL is due to an improvement of crystal structure; however, TEM results shown in Section 5.4 clearly show that the concentration of defects in Fe-doped GaN is greatly higher than the one of UID GaN (Sample A). Therefore, it is unlikely that the suppression of the YL is related to an increase of crystal quality.

5.7 Electrical characterisation

GaN thin films doped with small concentrations of transition metals (TMs) have recently attracted increasing attention in spintronic and electronic applications due to their unique electrical and magnetic properties. When a transition metal, such as Fe or Mn, is introduced in GaN structure, part of their d electrons is employed in sd^3 bonds and part remains unpaired, modifying the electromagnetic properties of the materials [79]. Further details about the influence of these TMs on the electrical structure of GaN are discussed in Chapter 1. Of particular interest for HEMT applications is the ability of the Fe impurities to compensate the unintentional n -type conductivity of GaN, generated by donor impurities, and to lead to semi-insulating behaviour. If a semi-insulating material is grown between the substrate and the GaN buffer layer, the insulation, and in turn the performance, of the devices improves, especially in high-power, high-frequency applications [87]. A common method used to improve the insulation level of HEMT device involves the introduction at the substrate interface of a highly-defective layer, in which threading dislocations are used as acceptors to compensate the background

conductivity. However, the growth of dislocation-based semi-insulating GaN is still empirical and can affect the structural and morphological properties of the buffer GaN layer grown above it [83]. Therefore, the use of TM-doping appears to be advantageous, since very low concentrations of TM atoms are expected to influence the electrical properties of GaN without lowering the structural quality [84]. Fe-doped GaN pseudo-substrates grown using MOCVD have already been experimented resulting in net improvement of mobility and carrier density of the final HEMT device [87]. However, Bonanni and collaborators [88] found an unexpected relation between the electrical properties and the secondary Fe-rich phases present in highly-doped GaN. Their results suggested that when the Fe concentration is higher than the solubility limit, the Fe-rich nanocrystals might influence the concentration of carrier in the thin film and reduce its resistivity [88]. Therefore, the investigation of the electrical properties of UID and Fe-doped GaN thin films under study, and the relation between these properties and the secondary phases observed in Sample C, were investigated and discussed in this section.

In this work electrical properties such as sheet carrier concentration (n_s) and sheet mobility (μ_s) were obtained using room-temperature Hall measurements. During this measurement the sample was loaded on a 4-probes card and the contacts are obtained by soldering the copper wires on In contacts. During the soldering In in fact reacts with GaN producing a thin InN layer that improves the ohmic contact. In Figure 5.15 the values of sheet carrier concentration (n_s) and sheet mobility (μ_s) of the thin films under study are plotted as a function of Fe concentration. Firstly, it is worth noticing that the electrical properties of UID GaN are surprisingly high, considering that the thin film is grown directly on sapphire without using any template that might improve the quality of the thin film. The Hall mobility and the carrier concentration of UID GaN, in fact, are measured to be 75 cm²/Vs and 3.5 x 10¹⁴ cm⁻², respectively. From these results it appears that GaN grown in Ga-rich conditions using e-beam PVD shows very promising properties for the growth of binary GaN and more complex GaN-based systems. Therefore, further optimisation might make e-beam PVD technique a valid alternative to grow III-nitride with relatively high quality.

In addition, from Figure 5.15a and b it is evident that the introduction of Fe in GaN structure reduces the conductivity of GaN. When the Fe concentration is increased from 0 to 4.6 %, in fact, the carrier concentration decreases of about 4 orders of magnitude from 3.5 x 10¹⁴ to 3 x 10¹⁰ cm⁻², while the resistivity increases from 1090 to 9.5 x 10⁸ Ωcm⁻².

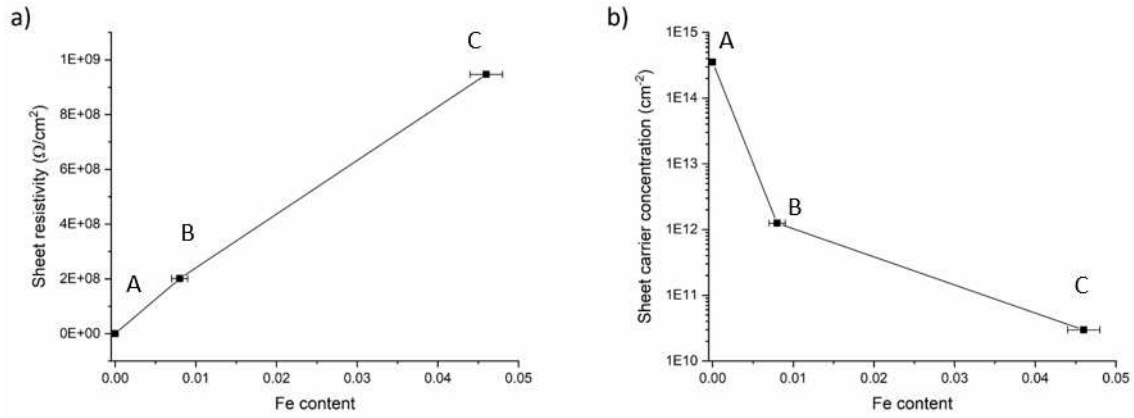


Figure 5.15 Sheet resistivity (a) and sheet carrier resistivity (b) plots of UID and Fe-doped GaN obtained from Hall measurements.

The high resistivity of Fe-doped GaN is related to the presence of acceptor-like states, introduced by Fe atoms. These acceptor-like states are able to compensate the free carriers generated by donor-impurities such as Si or oxygen and reduce the sheet carrier density of about 4 order of magnitude. In agreement with these results, the sheet resistivity also linearly increases up to $10^{10} \Omega\text{cm}^{-2}$ when the Fe concentration increases. It is interesting to notice that when the Fe concentration is as high as 4.6 %, the resistivity of the sample is comparable and even higher to that reported in the literature [84], despite the presence of secondary phases observed in TEM images. This discrepancy with Bonanni's results, might have two possible explanations. Bonanni and co-worker suggested that the increase of carrier concentration for high Fe contents could be related to the increase of oxygen impurities when the flow rate of ferrocene (Cp_2Fe) is increased [88]. Since in e-beam PVD the reactive Fe is obtained using a different source, it is possible that the oxygen impurities in the e-beam PVD thin films are maintained under control and are not dependent on the concentration of iron used. Another possible explanation is that the concentration of Fe in Sample C is not high enough to trigger the different electrical behaviour, and a reduction of resistivity might be observed if the Fe concentration in PVD samples is further increased. However, the inhomogeneity of the structure of this sample observed in TEM images and the linear correlation between resistivity and Fe concentration make this explanation unlikely. Further investigation of more heavily Fe-doped GaN and of the dependence of these electrical properties on the temperature might be useful to better understand the influence of the Fe-rich nanocrystals on the semi-insulating properties of these thin films.

5.8 Conclusions

In this chapter the structural, optical and electrical properties of unintentionally doped (UID) and Fe-doped GaN grown using e-beam PVD have been presented and discussed. First, STEM imaging and EDX maps were used to calculate the concentration of Fe in the doped samples and evaluate the

homogeneity in their structure. The sample grown using lower Fe e-beam current has a Fe concentration of 0.8 %, lower than the solubility limit, and its structure appears to be homogeneous (STEM images) with random distribution of Fe atoms (EDX maps). However, when the Fe e-beam current increases from 20 to 53 mA, the concentration of Fe is as high as 4.6 % and darker spherical regions becomes evident in the STEM image. Using low- and high-magnification EDX mapping it was concluded that the darker region were Fe-rich nanocrystals dispersed in the GaN matrix. Further investigation of these nanocrystals was carried out using HR-XRD, HR-TEM and diffraction patterns. From these characterisations, it was found that the nanocrystals are indeed Fe-rich and stable in α -Fe and Fe_xN secondary phases. The generation of these secondary phases is caused by the concentration of Fe atoms well above the solubility limit, so that the structure undergoes spinodal decomposition driven by the magnetic attraction of excessive Fe atoms dispersed in the matrix [72].

Morphological characterisation was also used to investigate the regime in which the growth took place. The surface of UID GaN was found relatively smooth with Ga droplets deposited on it, suggesting that the growth of this sample took place in Ga-droplet regime. However, when Fe is introduced the regime moved from Ga-rich to Ga-poor Metal-rich, as suggested by the small grains visible in AFM images. In this case, in fact, Fe atoms adsorb on the growing surface, destroying the Ga liquid bilayer, typical of Ga-rich conditions and reducing the mobility of Ga adatoms. Such that, the surface of Fe-doped GaN shows rougher morphology and small dots of unreacted Fe adsorbed on it.

In addition, the influence of Fe concentration on the crystal quality and the stress level in the thin films are fully investigated. In agreement with STEM and HR-TEM results, the rocking curves of the thin films become broader when the Fe concentration increases, suggesting that the introduction of Fe in the GaN matrix reduces the crystal quality of the thin films. Moreover, all thin films are found to be under in-plane compressive stress, and when the Fe concentration increases the stress level decreases, as suggested by the c/a ratios and Raman spectroscopy. This reduction of stress is believed to be related to a partial relaxation of strain via generation of defects, in agreement with TEM and HR-XRD results.

Finally, the optical and electrical properties of these thin films were investigated. The band gap is found to decrease from 3.37 to 3.33 eV when the Fe concentration increases from 0 to 4.6 %. This reduction is related to introduction of Fe-related acceptor-like states localised just below the bottom of the conduction band. These states are able to compensate the background carrier conductivity present in UID GaN leading to semi-insulating behaviour. This semi-insulating behaviour was confirmed by Hall results. When the Fe concentration is increased from 0 to 4.6 %, in fact, the carrier concentration reduces from 3.5×10^{14} to $3 \times 10^{10} \text{ cm}^{-2}$ and the resistivity increases from 1090 to $9.5 \times 10^8 \text{ }\Omega\text{cm}^2$. Moreover, no relation between electrical properties and secondary phases was observed and an increase of the resistivity of one order of magnitude was observed when the Fe levels was increased from 0.8 % (homogeneous structure) to 4.6 % (inhomogeneous structure).

These results are very promising for future employment of UID and Fe-doped GaN grown using e-beam PVD in HEMT fabrication process. The structural quality and the electrical properties, in fact, are found to be comparable to the ones reported in literature obtained using more optimised techniques. In particular it was found that introducing concentration of Fe as small as 0.8 % leads to resistivity as high as $2 \times 10^8 \Omega\text{cm}^{-2}$ without largely affecting the structural properties. Further optimisation of this thin films might give an alternative path to produce good-quality, highly-resistive substrate for GaN-based HEMT devices.

Chapter 6

Conclusions and future work

6.1 Conclusions

In this thesis e-beam physical vapour deposition (e-beam PVD) is proposed as alternative technique for the growth of III-nitride thin films and the characterisation of binary, scandium- and iron-based GaN is presented for the first time. These materials are of great interest for high electron mobility transistors (HEMTs) and the structural, optical and electrical properties relevant for HEMT devices were extensively studied using several different techniques.

Since e-beam PVD is not commonly used to grow GaN and other III-nitride materials, the properties of binary GaN, about 200 nm thick and grown directly on sapphire, are first investigated, and the results reported in Chapter 3. In order to find the optimal III/V ratio in the chosen growth conditions, GaN thin films were grown using increasing Ga e-beam current. A strict relation between Ga e-beam current used and growth rate measured is observed, suggesting that the growths take place in N-rich conditions. These N-rich conditions are also confirmed by the surface morphology observed in AFM images [165]. On the surface of all thin films under study, in fact, typical rounded nanocrystallites are observed, whose dimension depends on the Ga e-beam current used. This variation of nanocrystallite size suggests that when the Ga e-beam current increases, the crystal quality also increases, in agreement with HR-XRD

and TEM results. All results obtained from these thin films indicate a constant increasing of crystal quality when the Ga e-beam current increases from 76 mA to 82 mA, while for even higher e-beam currents the crystal quality drops again. The optical properties of these thin films, on the other hand, are found to be consistent throughout the dataset, and no strict relation with the used Ga e-beam current is observed. The band gap of these thin films was calculated using transmittance and photoluminescence spectra. In both cases the calculated band gap is much lower than the value reported in literature (3.4 eV) and equal to about 3.10 – 3.15 eV. This lower value is expected to be related to the high concentration of defects present in the structure, which makes the luminescence defect-dominant and reduces the band gap of the thin film.

According to these results, the optimal Ga e-beam current in these conditions is equal to 82 mA, since the resulting GaN thin film has the narrowest rocking curve (1.51°), the biggest nanocrystallites (60 nm) and qualitatively the lowest defect density. However, the densities of columnar misorientations and structural defects are still relatively high and, compared to more optimised techniques such as MOCVD, the quality of these thin films is still relatively low. Therefore, further optimisation of other growth conditions is necessary to make e-beam PVD a competitive growth technique. However, considering that these preliminary thin films were grown directly on sapphire and are only 200 nm thick, the properties observed in this work are very promising for future applications of e-beam PVD in GaN-based device growth, after proper optimisation. Moreover, if these thin films are compared with GaN results showed in Chapter 5, a large improvement of the system conditions is already evident within this thesis work. Therefore, further optimisation of the system might lead to GaN thin films showing competitive quality if compared with thin films grown using established systems such as MOCVD.

After the growth of binary GaN thin films, more complex systems were grown in the e-beam PVD system using a second e-beam gun loading scandium or iron. In the first case, ScGa_N thin films with increasing concentration of Sc are obtained. This relatively new transition metal (TM) based material is of particular interest for HEMT devices due to the large increase of piezoelectric polarisation and of the band gap when Sc is introduced in GaN structure [182]. The growth of homogenous, high-quality ScGa_N is however challenging, since binary GaN and ScN are stable in wurtzite and rock-salt structures, respectively. Therefore, if the Sc concentration is close to the solubility limit (~ 27 %) cubic inclusions are usually observed in the ScGa_N thin films [157].

In Chapter 4 ScGa_N thin films with increasing concentration of scandium grown on sapphire using e-beam PVD are investigated. The structural properties were comprehensively characterised using AFM, XRD, TEM and Raman spectroscopy; while the optical characterisation was carried out using Transmittance, Reflectance and Photoluminescence spectroscopies. The homogeneity of the structure and the concentration of Sc in the thin films were studied using SIMS. From SIMS and STEM results, no Sc-rich accumulation layers on the surface or at the substrate-interface, nor cubic inclusions were observed in ScGa_N thin films grown using e-beam PVD, even for the highest concentration of Sc (20 %). In addition, the absence of cubic inclusions was also confirmed using Raman spectroscopy. As

already observed in ScGa₂N grown using MBE [157], the growth rate was found strictly dependent on the Sc e-beam current used, and when Sc concentration is increased from 0 to 20 % the growth rate increases from 8 to 334 nm/h. This dependence is probably related to the catalytic reaction between molecular N₂ and Sc, which increases the concentration of reactive nitrogen and, in turn, the deposition rate of ScGa₂N [159]. This dependence, however, makes difficult to predict the regime in which the growth takes place, as well as the thickness of the resulting thin film. From AFM images it is evident that binary GaN is grown in N-rich conditions following a typical 3D nucleation mechanism. When Sc is introduced in the system, 3D nanocrystallites are still visible, suggesting that the growth of ternary ScGa₂N takes place in either N-rich or Ga-poor Metal rich-conditions [165]. However, due to the catalytic reaction taking place, it is difficult to predict the real concentration of nitrogen and confirm in which regime the thin films are grown. In addition, in AFM images a clear increase of nanocrystallite size from 40 to 80 nm is evident when the Sc concentration is increased from 0 to 20 %. This increase might be due to the higher concentration of Sc on the surface, which favours the diffusion of adatoms and prevents the accumulation of nitrogen on the surface of the growing thin film [165]. Another explanation for this increasing nanocrystallite size is that higher Sc concentrations lead to higher crystal quality. This possibility is also suggested by HR-XRD scans and TEM images. The FWHM of rocking curves decreases from 1.5 to 0.43 °, suggesting a large improvement of crystal quality when the Sc concentration is 20 %. In agreement with these results, both bright-field and high-resolution TEM images show that the defect density for this thin film is much lower than that of the other ScGa₂N thin films. To further investigate the structural properties of this thin film, HR-STEM images of ScGa₂N with the highest concentration of Sc were obtained, confirming the reduction of defect concentration for this sample. This large improvement of crystal quality might be related to the higher growth rate or to an unexpected relation between the lattice parameters a of sapphire and ScGa₂N with 20 % of Sc. If for instance the length of 4 unit cells of ScGa₂N is equal to the length of 3 sapphire unit cells, then the stress in the overall structure is partially released, and the generation of defects largely reduced. Unfortunately, in this work it was not possible to directly measure the lattice parameter a of ScGa₂N and a quantitative investigation of this relation could be performed in the future.

The band gap of these ScGa₂N thin films was calculated using Transmittance and Reflectance spectroscopy. In both cases, a clear increase of the band gap of about 0.3 eV is observed when the Sc concentration is increased from 0 to 20 %. This increase is in agreement with theoretical results [68] and previous investigations of high-quality ScGa₂N grown using MBE [66]. This enlargement of band gap is of particular interest for HEMT devices, in which the confinement of the channel is directly related to the band offset between GaN and ScGa₂N (or AlGa₂N). Finally, photoluminescence spectra were obtained for ScGa₂N and a large broad band at about 450 nm is observed in all samples. Since no variation is visible when the Sc concentration is increased from 0 to 20 %, the high intensity of this band and the quenching of the near-band-edge peak are believed to be caused by the relatively high concentration of defects in the structure. This defect concentration is probably related to the growth of

GaN and ScGaN directly on sapphire, without using any GaN-based template. Therefore, the growth of ScGaN on GaN thick template is expected to largely improve both the structural and optical properties of ScGaN thin films grown using e-beam PVD.

Compared to other techniques, e-beam PVD appears to be very promising for the growth of high-quality Sc-based GaN. The thin films reported in this work, in fact, are directly grown on sapphire and no template was used to improve their quality. Since the results of these thin films appear to be relatively comparable to those of ScGaN grown using MBE on GaN or AlN templates [66], it might be possible to obtain even better-quality ScGaN when these templates are employed in e-beam PVD growth. However, further optimisation of the growth conditions is first required.

Finally, the properties of iron-based GaN thin films grown using e-beam PVD are studied in this work. Fe-doped GaN has attracted increasing interest in HEMT device fabrication because of its semi-insulating properties. The addition of a Fe-doped GaN layer between the substrate and the buffer layer reduces the background carrier concentration and improves the insulation of the transistor channel [87]. In Chapter 5 the structural, optical and electrical properties of Fe-doped GaN are fully investigated. First the homogeneity and the concentration of Fe were evaluated using STEM and TEM-EDX techniques. The thin film with lower concentration of Fe (0.8 ± 0.1 %) shows homogenous structure, while the sample with higher concentration of Fe (4.6 ± 0.2 %) has high concentration of nanocrystals dispersed in GaN matrix. From EDX maps it was found that the concentration of Fe in the nanocrystal is much higher than in the rest of the structure and a strict relation between Fe-rich and Ga-poor regions is also visible. These observations suggest that when the iron concentration is lower than the solubility limit Fe can substitute Ga and be homogeneously dispersed in GaN matrix; when its concentration is higher than the limit, then spinodal decomposition occurs, generating Fe-rich and Fe-poor regions in the structure. This behaviour was already observed in Fe-doped GaN grown using MOCVD and other TM-based GaN [72]. Further investigation of the nature of the nanocrystal was carried out using XRD and HR-TEM images. From the 2θ - ω scans and the d spacing measured in TEM images, it was found that the excess of Fe in GaN matrix precipitates as α -Fe and ζ -Fe₂N [175]. The lower crystal quality of Fe-doped GaN with higher concentration of Fe was also confirmed by Raman spectra. Additional peaks due to defects and relaxation of Raman selection-rules, in fact, were visible in the Raman spectrum of GaN thin film doped with 4.6 % of Fe.

The growth regime of these thin films was also investigated using AFM: while the morphology of binary GaN suggests that this thin film is grown in Ga-droplet regime, the Fe-doped thin films appears to be grown in Ga-poor metal-rich regime, according to Haider's model [165]. Further structural characterisation of undoped and Fe-doped GaN grown in these conditions was carried out using XRD rocking curves. It was found that both binary GaN and Fe-doped GaN with lower concentration of Fe show relatively high-crystal quality with rocking curve as narrow as 0.38 and 0.67° , respectively. These

results are very promising for the growth of high-quality GaN and GaN-based systems in metal-rich conditions using e-beam PVD as alternative growth technique.

The band gap of these thin films was also calculated using Transmittance and Photoluminescence techniques. In both cases the band gap decreases when the Fe concentration increases, due to the introduction of Fe-related acceptor-like states below the bottom of the conduction band. These acceptor-like states are able to compensate the net background carrier concentration introduced in GaN structure by donor impurities, such as silicon and oxygen, leading to semi-insulating behaviour of doped GaN thin films. This semi-insulating behaviour was investigated using Hall measurements, and a reduction of carrier concentration of 4 order of magnitude was observed when Fe concentration is increased from 0 to 4.6 %, while the resistivity increases up to $9.5 \times 10^8 \Omega\text{cm}^{-2}$. In addition, no relation between Fe-rich nanocrystals and electrical properties was observed, in contrast with Fe-doped GaN grown using MOCVD. In that case, in fact, when Fe concentration was higher than the solubility limit, an increment of carrier concentration was observed [88]. The structural and electrical properties observed for Fe-doped GaN grown using e-beam PVD are promising for a possible future use of e-beam PVD as alternative technique for the growth of high-quality highly-resistive Fe-doped GaN pseudo-substrates for HEMT devices.

6.2 Future work

The results reported in this thesis may pave the way for future work on both the investigation of material properties grown using e-beam PVD and on the application in HEMT device fabrication of the scandium- and iron-based GaN thin films studied in this work.

Regarding the employment of e-beam PVD as alternative technique for the growth of III-nitrides, further optimisation of e-beam PVD growth variables, such as substrate temperature (T_s) or nitrogen partial pressure (p_{N_2}), might lead to binary GaN with improved crystal quality, especially if grown in Ga-rich conditions, as shown in Chapter 5.

ScGa_{0.2}N grown using e-beam PVD showed surprisingly good crystal quality, no cubic inclusions dispersed in the structure and larger band gap than binary GaN. Future investigation of the lattice parameter of ScGa_{0.2}N with 20 % of Sc might give more quantitative insights about the relation between ScGa_{0.2}N and sapphire lattice parameters and about the strain level present in this structure. In addition, future growths of these thin films on high-quality GaN templates might lead to large improvement of ScGa_{0.2}N crystal structure. If these templates are used, the concentration of defects might reduce leading to improved optical properties and even larger band gaps when the concentration of Sc is increased.

These properties are very interesting for the fabrication of alternative HEMT devices, in which the active layer AlGa_{0.3}N is substituted by ScGa_{0.2}N. The 2D channel of the transistor, in fact, rises at the interface between GaN and ScGa_{0.2}N (or AlGa_{0.3}N), and concentration and mobility of the carriers in the channel strictly depend on the band offset and the polarisation level of the active layer. Therefore, future

studies of spontaneous and piezoelectric polarisation in ScGa₂N and ScGa₂N/GaN interfaces might give useful information for the growth of alternative ScGa₂N-based HEMT devices. In addition, the polarity of both the buffer (GaN) and the active (ScGa₂N) layer deeply influences the properties of the final HEMT device [9], [23]. Therefore, polarity of ScGa₂N grown using e-beam PVD should be investigated in the future. In scandium-based system, however, this investigation might be challenging: the polarity is in fact generally investigated using KOH/NaOH etching, in which Sc and Ga react very differently, generating misleading results [183], [184]. For this purpose, electron backscattering and convergent electron beam diffraction might be employed as alternative techniques [185], [186].

Moreover, the ScGa₂N thin films studied in this work have all Sc concentration not higher than 20 %. However, theoretical calculations suggest that the wurtzite structure should be stable for Sc concentrations up to 27 % [68]. Therefore, future investigation of the properties of ScGa₂N with Sc concentration between 20 and 27 % might give interesting information about the structural and electrical properties of ScGa₂N with Sc content closer to the transition point. In addition, in this work the content of Sc was calculated using SIMS and MOCVD GaN as standard. However, calculation of models of the relative intensities of Sc- and Ga-EDX peaks might give a reliable tool to calculate the content of Sc directly from STEM images. In addition, the use of standard techniques such as RBS (Rutherford backscattering spectrometry) would give an indication of the accuracy of the Sc content calculated using both SIMS and EDX [162].

Finally, Fe-doped GaN thin films were grown using e-beam PVD and characterised in this work. However, the study of intermediate concentrations between 0.8 and 4.6 % would give more accurate value of the highest Fe concentration that can be homogeneously dispersed in GaN without generation of Fe-rich nanocrystals. Further investigation of electrical properties of these thin films and their dependence on the temperature might also give useful information to understand the influence of Fe-rich nanocrystal on the electrical properties of these thin film. In addition, the study of GaN doped with Fe concentrations below 0.8 % will be useful to find the optimal thin film showing resistivity of the order of $10^8 \Omega\text{cm}^2$ with rocking curves narrower than 0.67° . These results are of particular interest for HEMT device used in high-power high-frequency applications. Possible leakage and dirt present in the MOCVD or MBE growth systems are believed to introduce donor impurities, such as oxygen or Si, that generate an unwanted *n*-type conductivity that deteriorate the performance of the device. The introduction of an additional insulating thin film on the top of the substrate would be able to compensate this conductivity and improve the performance of the final device [81]. However, the introduction of this additional layer cannot lower the structural quality of the device. Therefore, structural characterisation of GaN and (Fe,Ga)₂N/GaN structure grown in similar conditions should be carried out to confirm that the introduction of the semi-insulating layer does not reduce the quality of the entire structure.

Similar unwanted background conductivity was also observed in ScGa₂N, due to the presence of impurities incorporated during the growth. Therefore, to further improve the performance of alternative

ScGa₂N₃-based HEMT devices, quaternary FeScGa₂N₃ might be investigated as alternative active layer. The careful co-doping of Sc and Fe may lead to a quaternary material that shows intermediate behaviour between ternary ScGa₂N₃ and ternary (Fe,Ga)₂N₃. If fine control of the growth conditions is achieved, it might be possible to grow a transition metal nitride showing the piezoelectric properties of ScGa₂N₃ and the semi-insulating properties of (Fe,Ga)₂N₃, while retaining the large band offset with GaN. If these intermediate properties were achieved, FeScGa₂N₃ could be of great interest for electronic applications, such as HEMTs. The use of FeScGa₂N₃/GaN interface in a HEMT device, in fact, could improve the concentration and mobility of the carriers in the 2DEG channel as well as the confinement of the carriers in the channel. However, no theoretical or experimental results are currently available to confirm this hypothesis and future work is necessary to investigate this possibility.

Finally, from the results obtained in this work of binary GaN and scandium- and iron-based GaN, it appears to be worth investigating different III-nitrides, such as AlN, InN or more complex ternary and quaternary systems grown using e-beam PVD as alternative growth technique.

References

- [1] P. Siffert and E. F. Krimmel, “Silicon: evolution and future of a technology,” in *Springer-Verlag Berlin Heidelberg*, Springer Berlin Heidelberg, 2004.
- [2] M. S. Adler, K. W. Owyang, B. Jayant Baliga, and R. A. Kokosa, “The Evolution of Power Device Technology,” *IEEE Trans. Electron Devices*, vol. 31, no. 11, pp. 1570–1591, Nov. 1984.
- [3] H. Okumura, “Present status and future prospect of widegap semiconductor high-power devices,” *Japanese Journal of Applied Physics, Part 1: Regular Papers and Short Notes and Review Papers*, vol. 45, no. 10 A, pp. 7565–7586, 2006.
- [4] T. Mimura, “The early history of the high electron mobility,” *IEEE Trans. Microw. Theory Tech.*, vol. 50, no. 3, pp. 780–782, Mar. 2002.
- [5] E. Johnson, “Physical limitations on frequency and power parameters of transistors,” in *IRE International Convention Record*, 1966, vol. 13, pp. 27–34.
- [6] R. W. Keyes, “Figure of merit for semiconductors for high-speed switches,” *Proc. IEEE*, vol. 60, no. 2, p. 225, 1972.
- [7] B. J. Baliga, “Semiconductors for high-voltage, vertical channel field-effect transistors,” *J. Appl. Phys.*, vol. 53, no. 3, pp. 1759–1764, Mar. 1982.
- [8] B. J. Baliga, “Power Semiconductor Device Figure of Merit for High-Frequency Applications,” *IEEE Electron Device Lett.*, vol. 10, no. 10, pp. 455–457, Oct. 1989.
- [9] A. S. S. A. Fletcher and D. Nirmal, “A survey of Gallium Nitride HEMT for RF and high power applications,” *Superlattices and Microstructures*, vol. 109, Academic Press, pp. 519–537, 01-Sep-2017.
- [10] H. Sarbishaei, D. Y. T. Wu, and S. Boumaiza, “Linearity of GaN HEMT RF power amplifiers-A circuit perspective,” in *IEEE MTT-S International Microwave Symposium Digest*, 2012, pp. 1–3.
- [11] Y. Ohno and M. Kuzuhara, “Application of GaN-based heterojunction FETs for advanced wireless communication,” *IEEE Trans. Electron Devices*, vol. 48, no. 3, pp. 517–523, Mar. 2001.
- [12] T. Yamasaki *et al.*, “A 68% efficiency, C-band 100W GaN power amplifier for space applications,” in *IEEE MTT-S International Microwave Symposium Digest*, 2010, pp. 1384–1387.
- [13] B. (Bernard) Gil, *Low-dimensional nitride semiconductors*. Oxford University Press, 2002.

- [14] T. Sugahara *et al.*, “Direct evidence that dislocations are non-radiative recombination centers in GaN,” *Jpn. J. Appl. Phys.*, vol. 37, no. 4A, pp. L398–L400, Apr. 1998.
- [15] Z. Bougrioua *et al.*, “Engineering of-an insulating buffer and use of AlN interlayers: Two optimisations for AlGa_N-Ga_N HEMT-like structures,” in *Physica Status Solidi (A) Applied Research*, 2003, vol. 195, no. 1 SPEC, pp. 93–100.
- [16] Y. Li *et al.*, “Defect-reduced green GaInN/GaN light-emitting diode on nanopatterned sapphire,” *Appl. Phys. Lett.*, vol. 98, no. 15, p. 151102, Apr. 2011.
- [17] S. J. Cai *et al.*, “Annealing behavior of a proton irradiated Al_xGa_{1-x}N/GaN high electron mobility transistor grown by MBE,” *IEEE Trans. Electron Devices*, vol. 47, no. 2, pp. 304–307, 2000.
- [18] Y. Cai, Y. Zhou, K. J. Chen, and K. M. Lau, “High-Performance Enhancement-Mode AlGa_N / Ga_N HEMTs Using Fluoride-Based Plasma Treatment,” *Electron Device Lett. IEEE*, vol. 26, no. 7, pp. 435–437, Jul. 2005.
- [19] J. Tang *et al.*, “AlGa_N/AlN/GaN/InGa_N/Ga_N DH-HEMTs with improved mobility grown by MOCVD,” in *International Conference on Solid-State and Integrated Circuits Technology Proceedings, ICSICT*, 2008, pp. 1114–1117.
- [20] J. Kong, M. Feng, J. Cai, H. Wang, H. Wang, and H. Yang, “Ga_N grown on nano-patterned sapphire substrates,” *J. Semicond.*, vol. 36, no. 4, p. 043003, Apr. 2015.
- [21] M. A. Moram and S. Zhang, “ScGa_N and ScAlN: Emerging nitride materials,” *J. Mater. Chem. A*, vol. 2, no. 17, pp. 6042–6050, 2014.
- [22] I. Belabbas, P. Ruterana, J. Chen, and G. Nouet, “The atomic and electronic structure of dislocations in Ga based nitride semiconductors,” *Philos. Mag.*, vol. 86, no. 15, pp. 2241–2269, May 2006.
- [23] S. Helkman, S. Keller, Y. Wu, J. S. Speck, S. P. DenBaars, and U. K. Mishra, “Polarization effects in AlGa_N/Ga_N and Ga_N/AlGa_N/Ga_N heterostructures,” *J. Appl. Phys.*, vol. 93, no. 12, pp. 10114–10118, 2003.
- [24] F. Bernardini, V. Fiorentini, and D. Vanderbilt, “Spontaneous polarization and piezoelectric constants of III-V nitrides,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 56, no. 16, pp. R10024–R10027, 1997.
- [25] H. Qin, X. Luan, C. Feng, D. Yang, and G. Zhang, “Mechanical, thermodynamic and electronic properties of wurtzite and zinc-blende Ga_N crystals,” *Materials (Basel)*, vol. 10, no. 12, p. 1419, Dec. 2017.
- [26] P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, J. Neugebauer, and M. Scheffler, “Consistent set of band parameters for the group-III nitrides AlN, Ga_N, and InN,” *Phys. Rev. B - Condens. Matter*

Mater. Phys., vol. 77, no. 7, p. 075202, 2008.

- [27] J. Singh, *Electronic and optoelectronic properties of semiconductor structures*. Cambridge University Press, 2003.
- [28] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan, “Band parameters for III-V compound semiconductors and their alloys,” *J. Appl. Phys.*, vol. 89, no. 11 I, pp. 5815–5875, Jun. 2001.
- [29] S. Nakamura, T. Mukai, and M. Senoh, “Candela-class high-brightness InGaN/AlGaN double-heterostructure blue-light-emitting diodes,” *Appl. Phys. Lett.*, vol. 64, no. 13, pp. 1687–1689, Mar. 1994.
- [30] S. Nakamura, “The roles of structural imperfections in InGaN-based blue light- emitting diodes and laser diodes,” *Science*, vol. 281, no. 5379. American Association for the Advancement of Science, pp. 956–961, 14-Aug-1998.
- [31] S. Nakamura, S. Pearton, and G. Fasol, “*The Blue Laser Diode. The Complete Story.*” Springer, 2000.
- [32] S. Zhang, D. Holec, W. Y. Fu, C. J. Humphreys, and M. A. Moram, “Tunable optoelectronic and ferroelectric properties in Sc-based III-nitrides,” *J. Appl. Phys.*, vol. 114, no. 13, p. 133510, Oct. 2013.
- [33] J. Sumner, R. A. Oliver, M. J. Kappers, and C. J. Humphreys, “Scanning capacitance microscopy studies of unintentional doping in epitaxial lateral overgrowth GaN,” *J. Appl. Phys.*, vol. 106, no. 10, p. 104503, Nov. 2009.
- [34] T. Zhu, M. J. Kappers, M. A. Moram, and R. A. Oliver, “Quantification of unintentional doping in non-polar GaN using scanning capacitance microscopy,” in *Physica Status Solidi (C) Current Topics in Solid State Physics*, 2010, vol. 7, no. 7–8, pp. 1875–1877.
- [35] J. Sumner, S. Das Bakshi, R. A. Oliver, M. J. Kappers, and C. J. Humphreys, “Unintentional doping in GaN assessed by scanning capacitance microscopy,” in *Physica Status Solidi (B) Basic Research*, 2008, vol. 245, no. 5, pp. 896–898.
- [36] S. Nakamura, T. Mukai, and M. Senoh, “Si- and Ge-Doped GaN Films Grown with GaN Buffer Layers,” *Jpn. J. Appl. Phys.*, vol. 31, no. 9 R, pp. 2883–2888, Sep. 1992.
- [37] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, “P-type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI),” *Jpn. J. Appl. Phys.*, vol. 28, no. 12 A, pp. L2112–L2114, Dec. 1989.
- [38] K. S. Kim *et al.*, “Codoping characteristics of Zn with Mg in GaN,” *Appl. Phys. Lett.*, vol. 77, no. 8, pp. 1123–1125, Aug. 2000.
- [39] R. G. Wilson, S. J. Pearton, C. R. Abernathy, and J. M. Zavada, “Thermal stability of implanted dopants

- in GaN,” *Appl. Phys. Lett.*, vol. 66, no. 17, pp. 2238–2240, Apr. 1995.
- [40] R. Zhang and T. F. Kuech, “Photoluminescence of carbon in situ doped GaN grown by halide vapor phase epitaxy,” *Appl. Phys. Lett.*, vol. 72, no. 13, pp. 1611–1613, Jul. 1998.
 - [41] S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, “Thermal annealing effects on P-type Mg-doped GaN films,” *Jpn. J. Appl. Phys.*, vol. 31, no. 2, pp. 139–142, Feb. 1992.
 - [42] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, “Hole Compensation Mechanism of P-Type GaN Films,” *Jpn. J. Appl. Phys.*, vol. 31, no. 5 R, pp. 1258–1266, May 1992.
 - [43] Y. Y. Wong *et al.*, “Growth and fabrication of AlGaIn/GaN HEMT on SiC substrate,” in *2012 10th IEEE International Conference on Semiconductor Electronics, ICSE 2012 - Proceedings*, 2012, pp. 729–732.
 - [44] A. Krost and A. Dadgar, “GaN-based optoelectronics on silicon substrates,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 93, no. 1–3, pp. 77–84, 2002.
 - [45] W. A. Melton and J. I. Pankove, “GaN growth on sapphire,” *J. Cryst. Growth*, vol. 178, no. 1–2, pp. 168–173, 1997.
 - [46] S. Zhang, W. Y. Fu, D. Holec, C. J. Humphreys, and M. A. Moram, “Elastic constants and critical thicknesses of ScGaIn and ScAlIn,” *J. Appl. Phys.*, vol. 114, no. 24, p. 243516, 2013.
 - [47] S. L. Rhode *et al.*, “Structure and strain relaxation effects of defects in In_xGa_{1-x}N epilayers,” *J. Appl. Phys.*, vol. 116, no. 10, p. 103513, Sep. 2014.
 - [48] M. A. Moram *et al.*, “On the origin of threading dislocations in GaN films,” *J. Appl. Phys.*, vol. 106, no. 7, p. 073513, Oct. 2009.
 - [49] F. A. Ponce, D. Cherns, W. T. Young, and J. W. Steeds, “Characterization of dislocations in GaN by transmission electron diffraction and microscopy techniques,” *Appl. Phys. Lett.*, vol. 69, no. 6, pp. 770–772, Jun. 1996.
 - [50] D. N. Zakharov, Z. Liliental-Weber, B. Wagner, Z. J. Reitmeier, E. A. Preble, and R. F. Davis, “Structural TEM study of nonpolar a-plane gallium nitride grown on (1120)4H-SiC by organometallic vapor phase epitaxy,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 71, no. 23, p. 235334, Jun. 2005.
 - [51] V. Potin, P. Ruterana, and G. Nouet, “HREM study of stacking faults in GaN layers grown over sapphire substrate,” *J. Phys. Condens. Matter*, vol. 12, no. 49, p. 10301, 2000.
 - [52] Y. Zhong, X. H. Xia, F. Shi, J. Y. Zhan, J. P. Tu, and H. J. Fan, “Transition metal carbides and nitrides in energy storage and conversion,” *Advanced Science*, vol. 3, no. 5, 2015.

- [53] S. T. Oyama, "Introduction to the chemistry of transition metal carbides and nitrides," in *The Chemistry of Transition Metal Carbides and Nitrides*, Blackie Academic, 1996, pp. 1–27.
- [54] J. G. Chen, "Carbide and Nitride Overlayers on Early Transition Metal Surfaces: Preparation, Characterization, and Reactivities," *Chem. Rev.*, vol. 96, no. 4, pp. 1477–1498, 1996.
- [55] R. S. Ningthoujam and N. S. Gajbhiye, "Synthesis, electron transport properties of transition metal nitrides and applications," *Prog. Mater. Sci.*, vol. 70, pp. 50–154, May 2015.
- [56] P. Eklund, S. Kerdsonpanya, and B. Alling, "Transition-metal-nitride-based thin films as novel energy harvesting materials," *Journal of Materials Chemistry C*, vol. 4, no. 18, pp. 3905–3914, 2016.
- [57] M. A. Moram, Z. H. Barber, C. J. Humphreys, T. B. Joyce, and P. R. Chalker, "Young's modulus, Poisson's ratio, and residual stress and strain in (111)-oriented scandium nitride thin films on silicon," *J. Appl. Phys.*, vol. 100, no. 2, p. 023514, Jul. 2006.
- [58] H. A. Al-Brithen, A. R. Smith, and D. Gall, "Surface and bulk electronic structure of ScN(001) investigated by scanning tunneling microscopy/spectroscopy and optical absorption spectroscopy," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 70, no. 4, p. 045303, Jul. 2004.
- [59] D. Gall *et al.*, "Electronic structure of ScN determined using optical spectroscopy, photoemission, and ab initio calculations," *Phys. Rev. B*, vol. 63, no. 12, p. 125119, Mar. 2001.
- [60] M. G. Moreno-Armenta and G. Soto, "Electronic structure of scandium nitride with nitrogen and scandium deficits," *Comput. Mater. Sci.*, vol. 40, no. 2, pp. 275–281, Aug. 2007.
- [61] N. Takeuchi, "First-principles calculations of the ground-state properties and stability of ScN," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 65, no. 4, p. 045204, Jan. 2002.
- [62] N. Farrer and L. Bellaiche, "Properties of hexagonal ScN versus wurtzite GaN and InN," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 66, no. 20, pp. 2012031–2012034, Nov. 2002.
- [63] V. Ranjan, L. Bellaiche, and E. J. Walter, "Strained Hexagonal ScN: A Material with Unusual Structural and Optical Properties," *Phys. Rev. Lett.*, vol. 90, no. 25, p. 4, Jun. 2003.
- [64] C. Constantin *et al.*, "Composition-dependent structural properties in ScGaN alloy films: A combined experimental and theoretical study," *Journal of Applied Physics*, vol. 98, no. 12, American Institute of Physics, p. 123501, 15-Dec-2005.
- [65] H. C. L. Tsui *et al.*, "Valence band offsets of Sc_xGa_{1-x}N/AlN and Sc_xGa_{1-x}N/GaN heterojunctions," *J. Phys. D: Appl. Phys.*, vol. 49, no. 26, p. 265110, 2016.
- [66] H. C. L. Tsui *et al.*, "Band gaps of wurtzite Sc_xGa_{1-x}N alloys," *Appl. Phys. Lett.*, vol. 106, no. 13, p. 132103, Mar. 2015.

- [67] M. E. Little and M. E. Kordes, “Band-gap engineering in sputter-deposited $\text{Sc}_x\text{Ga}_{1-x}\text{N}$,” *Appl. Phys. Lett.*, vol. 78, no. 19, pp. 2891–2892, May 2001.
- [68] C. Constantin, H. Al-Brithen, M. B. Haider, D. Ingram, and A. R. Smith, “ScGa_{1-x}N alloy growth by molecular beam epitaxy: Evidence for a metastable layered hexagonal phase,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 70, no. 19, p. 193309, Nov. 2004.
- [69] A. Alsaad and A. Ahmad, “Optical and piezoelectric anomalies of ordered (Sc, Ga) N and (Sc, In) N ternaries,” *Eur. Phys. J. B*, vol. 65, no. 1, pp. 65–77, Sep. 2008.
- [70] F. Tasnádi *et al.*, “Origin of the Anomalous Piezoelectric Response in Wurtzite $\text{Sc}_x\text{Al}_{(1-x)}\text{N}$ Alloys,” *Phys. Rev. Lett.*, vol. 104, no. 13, p. 137601, Apr. 2010.
- [71] A. M. Alsaad and A. A. Ahmad, “Structural phase transitions and piezoelectric anomalies in ordered Sc_{0.5}Ga_{0.5}N alloys,” *Bull. Mater. Sci.*, vol. 30, no. 4, pp. 407–413, 2007.
- [72] A. Bonanni and T. Dietl, “A story of high-temperature ferromagnetism in semiconductors,” *Chemical Society Reviews*, vol. 39, no. 2. The Royal Society of Chemistry, pp. 528–539, 28-Jan-2010.
- [73] S. A. Wolf *et al.*, “Spintronics: A spin-based electronics vision for the future,” *Science*, vol. 294, no. 5546, pp. 1488–1495, 16-Nov-2001.
- [74] T. Dietl, “Nitrides as spintronic materials,” in *Physica Status Solidi (B) Basic Research*, 2003, vol. 240, no. 2, pp. 433–439.
- [75] H. Ohno, “Making nonmagnetic semiconductors ferromagnetic,” *Science*, vol. 281, no. 5379. American Association for the Advancement of Science, pp. 951–956, 14-Aug-1998.
- [76] T. Dietl, H. Ohno, and F. Matsukura, “Hole-mediated ferromagnetism in tetrahedrally coordinated semiconductors,” *Phys. Rev. B*, vol. 63, no. 19, p. 195205, Apr. 2001.
- [77] C. Liu, F. Yun, and H. Morkoç, “Ferromagnetism of ZnO and GaN: A Review,” *Journal of Materials Science: Materials in Electronics*, vol. 16, no. 9. Kluwer Academic Publishers, pp. 555–597, Sep-2005.
- [78] E. Malguth, A. Hoffmann, and M. R. Phillips, “Fe in III-V and II-VI semiconductors,” *Phys. Status Solidi Basic Res.*, vol. 245, no. 3, pp. 455–480, 2008.
- [79] A. Bonanni, “Ferromagnetic nitride-based semiconductors doped with transition metals and rare earths,” *Semicond. Sci. Technol.*, vol. 22, no. 9, pp. R41–R56, Sep. 2007.
- [80] Z. Bougrioua, M. Azize, P. Lorenzini, M. Lügt, and H. Haas, “Some benefits of Fe doped less dislocated GaN templates for AlGa_{1-x}N/GaN HEMTs grown by MOVPE,” in *Physica Status Solidi (A) Applications and Materials Science*, 2005, vol. 202, no. 4, pp. 536–544.
- [81] M. Silvestri, M. J. Uren, and M. Kuball, “Iron-induced deep-level acceptor center in GaN/AlGa_{1-x}N high

- electron mobility transistors: Energy level and cross section,” *Appl. Phys. Lett.*, vol. 102, no. 7, p. 073501, Feb. 2013.
- [82] D. O. Dumcenco *et al.*, “Characterization of freestanding semi-insulating Fe-doped GaN by photoluminescence and electromodulation spectroscopy,” *J. Appl. Phys.*, vol. 109, no. 12, p. 123508, Jun. 2011.
 - [83] S. Heikman, S. Keller, S. P. Denbaars, and U. K. Mishra, “Growth of Fe doped semi-insulating GaN by metalorganic chemical vapor deposition,” *Appl. Phys. Lett.*, vol. 81, no. 3, pp. 439–441, Jul. 2002.
 - [84] J. A. Freitas, M. Gowda, J. G. Tischler, J. H. Kim, L. Liu, and D. Hanser, “Semi-insulating GaN substrates for high-frequency device fabrication,” *J. Cryst. Growth*, vol. 310, no. 17, pp. 3968–3972, Aug. 2008.
 - [85] B. Monemar and O. Lagerstedt, “Properties of VPE-grown GaN doped with Al and some iron-group metals,” *J. Appl. Phys.*, vol. 50, no. 10, pp. 6480–6491, Oct. 1979.
 - [86] R. Heitz *et al.*, “Excited states of Fe³⁺ in GaN,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 55, no. 7, pp. 4382–4387, 1997.
 - [87] W. Lee *et al.*, “Optimization of Fe doping at the regrowth interface of GaN for applications to III-nitride-based heterostructure field-effect transistors,” *Appl. Phys. Lett.*, vol. 90, no. 9, p. 093509, Feb. 2007.
 - [88] A. Bonanni *et al.*, “Paramagnetic GaN:Fe and ferromagnetic (Ga,Fe)N: The relationship between structural, electronic, and magnetic properties,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 75, no. 12, 2007.
 - [89] D. Holec, L. Zhou, R. Rachbauer, and P. H. Mayrhofer, “Alloying-related trends from first principles: An application to the Ti-Al-X-N system,” *J. Appl. Phys.*, vol. 113, no. 11, p. 113510, Mar. 2013.
 - [90] H. Akinaga *et al.*, “Growth and characterization of low-temperature grown GaN with high Fe doping,” *Appl. Phys. Lett.*, vol. 77, no. 26, pp. 4377–4379, 2000.
 - [91] G. Kunert *et al.*, “Ga_{1-x}Mn_xN epitaxial films with high magnetization,” *Appl. Phys. Lett.*, vol. 101, no. 2, p. 022413, Jul. 2012.
 - [92] M. Lampalzer *et al.*, “Overgrowth experiments of ferromagnetic (MnGa)As-cluster layers by MOVPE,” in *Journal of Crystal Growth*, 2003, vol. 248, no. SUPPL., pp. 474–478.
 - [93] V. Marghussian, “Magnetic Properties of Nano-Glass Ceramics,” in *Nano-Glass Ceramics*, Elsevier, 2015, pp. 181–223.
 - [94] W. Kim, H. J. Kang, S. K. Noh, J. Song, and C. S. Kim, “Magnetic and structural properties of Fe ion-

- implanted GaN,” *J. Magn. Magn. Mater.*, vol. 316, no. 2, pp. e199–e202, Sep. 2007.
- [95] A. Bonanni *et al.*, “Controlled Aggregation of Magnetic Ions in a Semiconductor: An Experimental Demonstration,” *Phys. Rev. Lett.*, vol. 101, no. 13, p. 135502, Sep. 2001.
- [96] H.-Y. Shih *et al.*, “Ultralow threading dislocation density in GaN epilayer on near-strain-free GaN compliant buffer layer and its applications in hetero-epitaxial LEDs,” *Sci. Rep.*, vol. 5, no. 1, p. 13671, Nov. 2015.
- [97] I. M. Watson, “Metal organic vapour phase epitaxy of AlN, GaN, InN and their alloys: A key chemical technology for advanced device applications,” *Coord. Chem. Rev.*, vol. 257, no. 13–14, pp. 2120–2141, Jul. 2013.
- [98] Z. Zhang, H. Fang, Q. Yao, H. Yan, and Z. Gan, “Species transport and chemical reaction in a MOCVD reactor and their influence on the GaN growth uniformity,” *J. Cryst. Growth*, vol. 454, pp. 87–95, Nov. 2016.
- [99] Z. Zhang, Z. Liu, and H. Fang, “Influences of growth parameters on the reaction pathway during GaN synthesis,” *J. Cryst. Growth*, vol. 482, pp. 44–55, Jan. 2018.
- [100] E. J. Thrush, *Monitoring MOVPE growth of GaN*. University of Cambridge Press, 2008.
- [101] P. Ruterana, M. Albrecht, and J. Neugebauer, “Nitride Semiconductors: Hand book on Materials and Devices,” pp. 3–527, 2003.
- [102] C. T. Foxon and O. H. Hughes, “The current status of plasma assisted MBE growth of group III-nitrides,” *J. Mater. Sci. Mater. Electron.*, vol. 9, no. 3, pp. 227–230, 1998.
- [103] M. M. Rahman and M. N. Hasan, “Compound Semiconductor Epitaxial Growth Techniques,” *Int. J. Thin. Fil. Sci. Tec. Int. J. Thin Film. Sci. Technol.*, vol. 5, no. 1, pp. 45–49, 2016.
- [104] N. Grandjean, J. Massies, F. Semond, S. Y. Karpov, and R. A. Talalaev, “GaN evaporation in molecular-beam epitaxy environment,” *Appl. Phys. Lett.*, vol. 74, no. 13, pp. 1854–1856, Mar. 1999.
- [105] E. J. Tarsa, B. Heying, X. H. Wu, P. Fini, S. P. DenBaars, and J. S. Speck, “Homoepitaxial growth of GaN under Ga-stable and N-stable conditions by plasma-assisted molecular beam epitaxy,” *J. Appl. Phys.*, vol. 82, no. 11, pp. 5472–5479, 1997.
- [106] W. C. Hughes, “Molecular beam epitaxy growth and properties of GaN films on GaN/SiC substrates,” *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 13, no. 4, p. 1571, Jul. 1995.
- [107] H. Morkoç, *Handbook of Nitride Semiconductors and Devices Vol. 1: Materials Properties, Physics and Growth*. Wiley-VCH, 2008.
- [108] E. Sarigiannidou *et al.*, “Intrinsic ferromagnetism in wurtzite (Ga, Mn)N semiconductor,” *Phys. Rev.*

- B*, vol. 74, no. 4, pp. 2–5, Jul. 2006.
- [109] S. M. Knoll, S. Zhang, T. B. Joyce, M. J. Kappers, C. J. Humphreys, and M. A. Moram, “Growth, microstructure and morphology of epitaxial ScGaN films,” *Phys. Status Solidi Appl. Mater. Sci.*, vol. 209, no. 1, pp. 33–40, 2012.
 - [110] E. Reinhold and J. Faber, “Large area electron beam physical vapor deposition (EB-PVD) and plasma activated electron beam (EB) evaporation — Status and prospects,” *Surf. Coat. Technol.*, vol. 206, pp. 1653–1659, 2011.
 - [111] J. Singh, F. Quli, D. E. Wokfe, and J. Schriempf, “An Overview: Electron Beam-Physical Vapor Deposition Technology-Present and Future Applications,” *Surf. Eng. Sci. Technol.*, pp. 59–74, 1999.
 - [112] T. Mimura, S. Hiyamizu, T. Fujii, and K. Nanbu, “A new field-effect transistor with selectively doped GaAs/n-Al_xGa_{1-x}As heterojunctions,” *Jpn. J. Appl. Phys.*, vol. 19, no. 5, pp. L225–L227, May 1980.
 - [113] O. Ambacher *et al.*, “Two dimensional electron gases induced by spontaneous and piezoelectric polarization in undoped and doped AlGaN/GaN heterostructures,” *J. Appl. Phys.*, vol. 87, no. 1, pp. 334–344, Dec. 2000.
 - [114] J. P. Ibbetson, P. T. Fini, K. D. Ness, S. P. DenBaars, J. S. Speck, and U. K. Mishra, “Polarization effects, surface states, and the source of electrons in AlGaN/GaN heterostructure field effect transistors,” *Appl. Phys. Lett.*, vol. 77, no. 2, pp. 250–252, Jun. 2000.
 - [115] B. Jacobs, M. C. J. C. M. Kramer, E. J. Geluk, and F. Karouta, “Optimisation of the Ti/Al/Ni/Au ohmic contact on AlGaN/GaN FET structures,” *J. Cryst. Growth*, vol. 241, no. 1–2, pp. 15–18, May 2002.
 - [116] U. K. Mishra, P. Parikh, and Yi-Feng Wu, “AlGaN/GaN HEMTs-an overview of device operation and applications,” *Proc. IEEE*, vol. 90, no. 6, pp. 1022–1031, Jun. 2002.
 - [117] J. Golio, *Microwave MESFETs and HEMTs*, vol. 35, no. 9. Artech House, 1991.
 - [118] Y. Lv, X. Song, Z. Zhang, X. Tan, Y. Fang, and Z. Feng, “Improved performance of scaled AlGaN/GaN HFETs by recessed gate,” in *2016 International Forum on Wide Bandgap Semiconductors China, IFWS 2016 - Conference Proceedings*, 2017, pp. 107–109.
 - [119] K. Shinohara *et al.*, “Scaling of gan hemts and schottky diodes for submillimeter-wave mmic applications,” *IEEE Trans. Electron Devices*, vol. 60, no. 10, pp. 2982–2996, Oct. 2013.
 - [120] H. Amano *et al.*, “The 2018 GaN power electronics roadmap,” *Journal of Physics D: Applied Physics*, vol. 51, no. 16. IOP Publishing, p. 163001, 25-Apr-2018.
 - [121] S. Strite, “GaN, AlN, and InN: A review,” *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.*, vol. 10, no. 4, p. 1237, Jul. 1992.

- [122] P. Eaton and P. West, *Atomic Force Microscopy*. 2010.
- [123] Australian Microscopy & Microanalysis Research Facility, “MyScope - Training for advanced research,” 2014. [Online]. Available: <http://www.ammrf.org.au/myscope>.
- [124] G. Binnig, C. F. Quate, and C. Gerber, “Atomic force microscope,” *Phys. Rev. Lett.*, vol. 56, no. 9, pp. 930–933, Mar. 1986.
- [125] D. Nečas and P. Klapetek, “Gwyddion: An open-source software for SPM data analysis,” *Central European Journal of Physics*, vol. 10, no. 1, pp. 181–188, 2012.
- [126] D. Brandon and W. D. Kaplan, *Microstructural Characterization of Materials*. 2008.
- [127] M. A. Moram and M. E. Vickers, “X-ray diffraction of III-nitrides,” *Reports Prog. Phys.*, vol. 72, no. 3, p. 036502, Mar. 2009.
- [128] B. Fultz and J. Howe, “Diffraction and the X-Ray Powder Diffractometer,” Springer, Berlin, Heidelberg, 2013, pp. 1–57.
- [129] D. B. Williams and C. B. Carter, *Transmission Electron Microscopy. A Textbook for Materials Science. Second edition*. Springer, 2009.
- [130] M. H. Wong, F. Wu, T. E. Mates, J. S. Speck, and U. K. Mishra, “Polarity inversion of N-face GaN by plasma-assisted molecular beam epitaxy,” *J. Appl. Phys.*, vol. 104, no. 9, p. 093710, Nov. 2008.
- [131] S. Fearn, *An introduction to time-of-flight secondary ion mass spectrometry (ToF-SIMS) and its application to materials science*. IOP Publishing, 2015.
- [132] J. A. N. T. Soares, “Introduction to optical characterization of materials,” in *Practical Materials Characterization*, New York, NY: Springer New York, 2014, pp. 43–92.
- [133] T. Owen, *Fundamentals of Modern UV-Visible Spectroscopy | Ultraviolet–Visible Spectroscopy*. Agilent Technologies, Germeany, 2000.
- [134] J. Tauc, “Optical properties and electronic structure of amorphous Ge and Si,” *Mater. Res. Bull.*, vol. 3, no. 1, pp. 37–46, 1968.
- [135] M. Nowak, B. Kauch, and P. Szperlich, “Determination of energy band gap of nanocrystalline SbSI using diffuse.pdf,” *Review of Scientific Instruments Applied Physics Letters Journal of Applied Physics Journal of Applied Physics Journal of Applied Physics Applied Physics Letters*, vol. 801, no. 10, pp. 46107–2042, 2009.
- [136] A. E. Morales, E. S. Mora, and U. Pal, “Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures,” *Rev. Mex. Fis.*, vol. 53, no. 5, pp. 18–22, 2007.

- [137] L. Bergman and J. L. McHale, *Handbook of Luminescent Semiconductor Materials*. CRC Press, 2012.
- [138] R. Dingle and M. Ilegems, “Donor-acceptor pair recombination in GaN,” *Solid State Commun.*, vol. 9, no. 3, pp. 175–180, Feb. 1971.
- [139] C. W. B. John R. Ferraro, Kazuo Nakamoto, *Introductory Raman Spectroscopy.*, vol. 36. Academic Press, 2003.
- [140] P. Vandenabeele, *Practical Raman Spectroscopy - An Introduction*. 2013.
- [141] H. Harima, “Properties of GaN and related compounds studied by means of Raman scattering,” *Journal of Physics Condensed Matter*, vol. 14, no. 38. pp. 967–993, 2002.
- [142] E. H. Hall, “On a New Action of the Magnet on the Electric Currents,” *Am. J. Math.*, vol. 2, no. 3, pp. 287–292, 1879.
- [143] M. J. Deen and F. Pascal, “Electrical characterization of semiconductor materials and devices - Review,” *Journal of Materials Science: Materials in Electronics*, vol. 17, no. 8. Kluwer Academic Publishers, pp. 549–575, Aug-2006.
- [144] “Lake Shore 7500/9500 Series Hall System User’s Manual.”
- [145] B. Heying, R. Averbeck, L. F. Chen, E. Haus, H. Riechert, and J. S. Speck, “Control of GaN surface morphologies using plasma-assisted molecular beam epitaxy,” *J. Appl. Phys.*, vol. 88, no. 82, pp. 1855–5472, 2000.
- [146] A. Kawaharazuka, T. Yoshizaki, T. Hiratsuka, and Y. Horikoshi, “Effect of surface Ga accumulation on the growth of GaN by molecular beam epitaxy,” *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 7, no. 2, pp. 342–346, Feb. 2010.
- [147] K. Shen, M. Jiang, H. Liu, H. Hsueh, R. Horng, and D. Wu, “Pulsed laser deposition of hexagonal GaN-on-Si (100) template for MOCVD applications,” *Opt. Express*, vol. 21, no. 22, pp. 26468–26474, Nov. 2013.
- [148] P. Kidd, *XRD of gallium nitride and related compounds: strain, composition and layer thickness*. Panalytical, 2009.
- [149] R. Swanepoel *et al.*, “Determination of the thickness and optical constants of amorphous silicon,” *J. Phys. E.*, vol. 16, no. 12, pp. 1214–1222, 1983.
- [150] E. Márquez, J. Ramírez-Malo, P. Villares, R. Jiménez-Garay, P. J. S. Ewen, and A. E. Owen, “Calculation of the thickness and optical constants of amorphous arsenic sulphide films from their transmission spectra,” *J. Phys. D. Appl. Phys.*, vol. 25, no. 3, pp. 535–541, Mar. 1992.
- [151] J. Szczyrbowski and A. Czapla, “Optical absorption in D.C. sputtered InAs films,” *Thin Solid Films*,

- vol. 46, no. 2, pp. 127–137, Oct. 1977.
- [152] L. Vriens and W. Rippens, “Optical constants of absorbing thin solid films on a substrate,” *Appl. Opt.*, vol. 22, no. 24, p. 4105, Dec. 1983.
 - [153] G. Yu *et al.*, “Optical properties of wurtzite structure GaN on sapphire around fundamental absorption edge (0.78–4.77 eV) by spectroscopic ellipsometry and the optical transmission method,” *Appl. Phys. Lett.*, vol. 70, no. 24, pp. 3209–3211, Jun. 1997.
 - [154] M. Julkarnain, N. Kamata, T. Fukuda, and Y. Arakawa, “Yellow luminescence band in undoped GaN revealed by two-wavelength excited photoluminescence,” *Opt. Mater. (Amst.)*, vol. 60, pp. 481–486, Oct. 2016.
 - [155] M. A. Reshchikov *et al.*, “Unusual luminescence lines in GaN,” *J. Appl. Phys.*, vol. 94, no. 9, pp. 5623–5632, 2003.
 - [156] G. Santana *et al.*, “Photoluminescence study of gallium nitride thin films obtained by infrared close space vapor transport,” *Materials (Basel)*, vol. 6, no. 3, pp. 1050–1060, Mar. 2013.
 - [157] H. C. L. Tsui *et al.*, “The effect of metal-rich growth conditions on the microstructure of $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ films grown using molecular beam epitaxy,” *Phys. Status Solidi Appl. Mater. Sci.*, vol. 212, no. 12, pp. 2837–2842, Dec. 2015.
 - [158] T. Böttcher *et al.*, “Incorporation of indium during molecular beam epitaxy of InGaN,” *Appl. Phys. Lett.*, vol. 73, no. 22, pp. 3232–3234, Nov. 1998.
 - [159] M. A. Moram, T. B. Joyce, P. R. Chalker, Z. H. Barber, and C. J. Humphreys, “Microstructure of epitaxial scandium nitride films grown on silicon,” *Appl. Surf. Sci.*, vol. 252, no. 24, pp. 8385–8387, Oct. 2006.
 - [160] Gatan, “EELS Atlas.” [Online]. Available: <http://www.eels.info/atlas>.
 - [161] A. V Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, and C. J. Powell, “NIST X-ray Photoelectron Spectroscopy Database,” *NIST Standard Reference Database 20, Version 4.1*, 2012. [Online]. Available: <http://srdata.nist.gov/xps/>.
 - [162] H. C. L. Tsui *et al.*, “Composition measurement of epitaxial $\text{Sc}_x\text{Ga}_{1-x}\text{N}$ films,” *Semicond. Sci. Technol.*, vol. 31, no. 6, p. 064002, Jun. 2016.
 - [163] K. Prabhakaran, T. G. Andersson, and K. Nozawa, “Nature of native oxide on GaN surface and its reaction with Al,” *Appl. Phys. Lett.*, vol. 69, no. 21, pp. 3212–3214, Jun. 1996.
 - [164] J. C. Vickerman and I. S. (Ian S. Gilmore, *Surface Analysis—The Principal Techniques*. Wiley, 2009.
 - [165] M. B. Haider *et al.*, “Ga/N flux ratio influence on Mn incorporation, surface morphology, and lattice

- polarity during radio frequency molecular beam epitaxy of (Ga,Mn)N,” *J. Appl. Phys.*, vol. 93, no. 9, pp. 5274–5281, May 2003.
- [166] C. Constantin, H. Al-brithen, M. B. Haider, D. C. Ingram, and A. R. Smith, “Mixing Rocksalt and Wurtzite Structure Binary Nitrides to Form Novel Ternary Alloys: ScGa_N and MnGa_N,” *Mat. Res. Soc. Symp. Proc.*, vol. 799, no. 001, pp. 1–6, 2004.
 - [167] H. C. L. Tsui *et al.*, “Composition measurement of epitaxial Sc_x Ga_{1-x} N films,” *Semicond. Sci. Technol.*, vol. 31, no. 6, p. 064002, Jun. 2016.
 - [168] J. Zhang, T. Ruf, M. Cardona, O. Ambacher, and M. Stutzmann, “Raman spectra of isotopic GaN,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 56, no. 22, pp. 14399–14406, 1997.
 - [169] T. Dietl *et al.*, “Spinodal nanodecomposition in semiconductors doped with transition metals,” *Rev. Mod. Phys.*, vol. 87, no. 4, pp. 1311–1377, 2015.
 - [170] S. Gupta, H. Kang, M. H. Kane, E. H. Park, and I. T. Ferguson, “Growth and magnetization study of transition metal doped GaN nanostructures,” in *Physica Status Solidi (C) Current Topics in Solid State Physics*, 2008, vol. 5, no. 6, pp. 1740–1742.
 - [171] M. H. Kane, S. Gupta, and I. T. Ferguson, “Rare Earth and Transition Metal Doping of Semiconductor Materials,” in *Transition metal and rare earth doping in GaN*, Woodhead Publishing, 2016, pp. 315–370.
 - [172] Z. K. Tao *et al.*, “Optical and magnetic properties of Fe-doped GaN diluted magnetic semiconductors prepared by MOCVD method,” *Chinese Phys. Lett.*, vol. 25, no. 4, pp. 1476–1478, 2008.
 - [173] “ICSD reference pattern n. 01-0723-2103.”
 - [174] A. Corrión, F. Wu, T. Mates, C. S. Gallinat, C. Poblenz, and J. S. Speck, “Growth of Fe-doped GaN by RF plasma-assisted molecular beam epitaxy,” *J. Cryst. Growth*, vol. 289, no. 2, pp. 587–595, 2006.
 - [175] A. Navarro-Quezada *et al.*, “Embedded magnetic phases in (Ga,Fe)N: Key role of growth temperature,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 81, no. 20, p. 205206, 2010.
 - [176] M. H. Kane *et al.*, “Comparative study of Mn and Fe incorporation into GaN by metalorganic chemical vapor deposition,” in *Physica Status Solidi (A) Applications and Materials Science*, 2007, vol. 204, no. 1, pp. 61–71.
 - [177] T. Kawashima, H. Yoshikawa, S. Adachi, S. Fuke, and K. Ohtsuka, “Optical properties of hexagonal GaN,” *J. Appl. Phys.*, vol. 82, no. 7, pp. 3528–3535, Jun. 1997.
 - [178] Y. Fang *et al.*, “Effect of Fe-doping on nonlinear optical responses and carrier trapping dynamics in GaN single crystals,” *Appl. Phys. Lett.*, vol. 107, no. 5, pp. 1–6, 2015.

- [179] R. Deng, K. Jiang, and D. Gall, “Optical phonon modes in Al_{1-x}Sc_xN,” in *Journal of Applied Physics*, 2014, vol. 115, no. 1, p. 013506.
- [180] M. A. Reshchikov *et al.*, “Luminescence properties of defects in ZnO,” *Phys. B Condens. Matter*, vol. 401–402, no. 6, pp. 358–361, 2007.
- [181] Z. H. Feng *et al.*, “Influence of Fe-doping on GaN grown on sapphire substrates by MOCVD,” *J. Cryst. Growth*, vol. 309, no. 1, pp. 8–11, 2007.
- [182] V. Ranjan, S. Bin-Omran, D. Sichuga, R. S. Nichols, L. Bellaiche, and A. Alsaad, “Properties of GaN/ScN and InN/ScN superlattices from first principles,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 72, no. 8, p. 085315, Aug. 2005.
- [183] Z. Gu *et al.*, “Defect-selective etching of scandium nitride crystals,” *J. Cryst. Growth*, vol. 293, no. 2, pp. 242–246, Aug. 2006.
- [184] D. Huang *et al.*, “Dependence of GaN polarity on the parameters of the buffer layer grown by molecular beam epitaxy,” *Appl. Phys. Lett.*, vol. 78, no. 26, pp. 4145–4147, Jun. 2001.
- [185] C. Jäger, E. Spiecker, J. P. Morniroli, and W. Jäger, “Polarity determination of III-V compound semiconductors by large-angle convergent beam electron diffraction,” *Ultramicroscopy*, vol. 92, no. 3–4, pp. 273–283, Aug. 2002.
- [186] C. Trager-Cowan *et al.*, “Characterization of nitride thin films by electron backscatter diffraction,” *J. Microsc.*, vol. 205, no. 3, pp. 226–230, Mar. 2002.

Appendix A

Growth conditions

The sample investigated in this work were grown using a Mantis e-beam PVD system in London Centre for Nanotechnologies (LCN) by Dr. Robert J. Davies and Dr. Bin Zou at Imperial College London. The details of the growth conditions used to obtain the thin films discussed in Chapter 3, 4 and 5 are listed in Table A.1, A.2 and A.3, respectively.

Sample name	Ga e-beam current	Growth time	Substrate temperature (C)	RF-plasma	Nitrogen partial pressure
Sample A	73 mA	90 min	800 °C	400 W	1 E-4 torr
Sample B	76 mA	90 min	800 °C	400 W	1 E-4 torr
Sample C	79 mA	90 min	800 °C	400 W	1 E-4 torr
Sample D	82 mA	90 min	800 °C	400 W	1 E-4 torr
Sample E	85 mA	90 min	800 °C	400 W	1 E-4 torr

Table A. 1 e-beam PVD growth conditions used to grow GaN using increasing Ga e-beam current (Chapter 3)

Sample name	Sc	Ga e-beam current	Sc e-beam current	Growth time	Substrate temperature (C)	RF-plasma	Nitrogen partial pressure
Sample A	0 %	65 mA	--	300 min	850 °C	350 W	1 E-4 torr
Sample B	2 %	52 mA	13 mA	30 min	850 °C	350 W	1 E-4 torr
Sample C	5 %	60 mA	16 mA	30 min	850 °C	350 W	1 E-4 torr
Sample D	15 %	65 mA	23 mA	60 min	850 °C	350 W	1 E-4 torr
Sample E	20 %	64 mA	24 mA	30 min	850 °C	350 W	1 E-4 torr

Table A. 2 e-beam PVD growth conditions used to grow ScGa₂N using increasing Sc e-beam current (Chapter 4)

Sample name	Fe	Ga e-beam current	Fe e-beam current	Growth time	Substrate temperature (C)	RF-plasma	Nitrogen partial pressure
Sample A	--	55 mA	--	120 min	800 °C	400 W	4.6 E-5 torr
Sample B	1 %	66 mA	20 mA	180 min	800 °C	400 W	5E-5 torr
Sample C	4.9 %	40 mA	56 mA	120 min	800 °C	400 W	4.7 E-5 torr

Table A. 3 e-beam PVD growth conditions used to grow ScGa₂N using increasing Fe e-beam current (Chapter 5)

Appendix B

TEM sample preparation

The TEM samples studied in this work were manually prepared in the Cambridge Centre for GaN laboratory in the Material department of University of Cambridge.

Semiconductor thin films can be studied using TEM microscope when they are thin enough to be electron-transparent. The ideal thickness of a TEM sample is usually between 500 and 50 nm, depending on the magnification. A TEM sample can be prepared in cross-section or plan-view geometry, depending on the type of information required.

Cross-sectional TEM samples studied in this work are obtained along the $[01\bar{1}0]$ and $[11\bar{2}0]$ zone axes. Firstly, two bars of about $2.5 \times 5 \mu\text{m}$ were cut so that the short edge of one bars is parallel to the $[01\bar{1}0]$ and the other to the $[11\bar{2}0]$ direction. These two bars are then cleaned in acetone and inspected for any scratches on the surface. After that, one film is covered with Araldite epoxy resin and glued together with the second bar so that the two films face each other. The two bars are then put under pressure to avoid any bubble in the glue line and heated at 130° for 1 hour. After heating a smaller bar of about $1.5 \times 2.5 \mu\text{m}$ was cut using a circular blade.

The sides of the small bars were then mechanically polished using diamond disks with decreasing particle sizes to obtain a flat and shiny surface, which was checked using optical microscope. Once one side was shiny enough, a molybdenum O-ring was glued on the shiny side using two small drops of epoxy glue and the sample was cured at 130° for 1 hour. After the heating treatment, the structure was turned upside-down and mechanically polished until it was about $30 \mu\text{m}$ thick. The thinning of the sample was obtained by polishing the sample down to $200 \mu\text{m}$ using a $30 \mu\text{m}$ diamond disc, then down to $100 \mu\text{m}$ using a $15 \mu\text{m}$ disc, and finally down to $30 \mu\text{m}$ with a $9 \mu\text{m}$ disc. The thickness of the sample was measured at every step by calculating the difference in high between the surface of the sample and the O-ring beneath it using the optical microscope. Once the sample was about $30 \mu\text{m}$ thick, the final polishing was carried out using a Gatan Precision Ion Polishing System (PIPS). The sample was gently polished at 5 keV at an angle of 7° from the top and the bottom of the sample using Argon guns. The PIPS was configured in double-modulation mode, so that the milling of the O-ring was prevented. Once a hole was formed in the middle of the TEM sample, final cleaning of the surface was carried out by milling first at 3 keV for 10 minutes, then 1 keV for 10 minutes and finally at 0.1 keV for another 10 minutes.

A similar procedure was used to prepare plan view TEM samples. In this case the sample was first cut in 2 x 2 μm square sample; then the face with the nitride film was glued on the molybdenum O-ring using epoxy resin. The sample was then cured at 130 ° for 1 hour. The sapphire-face of the sample was then mechanically polished using diamond discs with particle size of 30, 15 and 9 μm until it was about 30 μm thick. The sample was then glued on a PIPS holder so that the film faced the holder and remained protected from any milling. As in cross sectional preparation, the final milling was performed using the PIPS at 5 keV and Argon guns at + 7 °. No modulation was necessary in this case to prevent the destruction of the film. As from the previous case, final cleaning of the surface was carried out by milling at 3 keV for 10 minutes, 1 keV for 10 minutes and then at 0.1 keV for another 10 minutes.

Appendix C

Permission to reproduce third party work

Permissions to reproduce third party Figures:

Figure	Reference n.	Licence n. - notes
1.3	[25]	Permission granted w/o licence n.
1.4	[32]	Licence n. 4454250888895 Reprinted from S. Zhang, D. Holec, W. Y. Fu, C. J. Humphreys, and M. A. Moram, <i>J. Appl. Phys.</i> , vol. 114, no. 13, p. 133510, Oct. 2013. with the permission of AIP Publishing
1.5	[51]	Licence n. 4453580141298 Reprinted from V Potin <i>et al</i> 2000 <i>J. Phys.: Condens. Matter</i> 12 10301 DOI: https://doi.org/10.1088/0953-8984/12/49/332 © IOP Publishing. All rights reserved
1.6	[52]	Permission granted w/o licence n.
1.7	[62]	Licence n. RNP/18/O CT/008688 <i>Reprinted Figure with permission from N. Farrer, L. Bellaiche Phys. Rev. B, 66 pp. 201203-201206 (2002) Copyright 2002 by the American Physical Society</i> DOI: https://doi.org/10.1103/PhysRevB.66.201203
1.8	[32]	Licence n. 4454250888895 Reprinted from S. Zhang, D. Holec, W. Y. Fu, C. J. Humphreys, and M. A. Moram, <i>J. Appl. Phys.</i> , vol. 114, no. 13, p. 133510, Oct. 2013. with the permission of AIP Publishing
1.9	[64]	Licence n. 4454240778062 Reprinted from Constantin C, Haider M B, Ingram D, Smith A R, Sandler N, Sun K and Ordejon P 2005 <i>J. Appl. Phys.</i> 98 123501. with the permission of AIP Publishing

1.10	[32]	Licence n. 4454250888895 Reprinted from S. Zhang, D. Holec, W. Y. Fu, C. J. Humphreys, and M. A. Moram, <i>J. Appl. Phys.</i>, vol. 114, no. 13, p. 133510, Oct. 2013. with the permission of AIP Publishing
1.11	[32]	Licence n. 4454250888895 Reprinted from S. Zhang, D. Holec, W. Y. Fu, C. J. Humphreys, and M. A. Moram, <i>J. Appl. Phys.</i>, vol. 114, no. 13, p. 133510, Oct. 2013. with the permission of AIP Publishing
1.12a	[78]	Licence n. 4454251197006 Reprinted from E. Malguth, A. Hoffmann, M. R. Phillips, <i>physica status solidi (b)</i>, vol. 245, no. 3, p. 26, Feb 2008, with the permission of John Wiley and Sons Publishing.
1.12b	[82]	Licence n. 4454260400824 Reprinted from D.O. Dumcenco, S. Levchenko, Y.S. Huang, C.L. Reynolds, J.G. Reynolds, K.K. Tiong, T. Paskova, K.R. Evans, <i>J. Appl. Phys.</i>, vol. 109, p. 123508, Apr. 2011. with the permission of AIP Publishing
1.13a	[79]	Licence n. 4532040888170 Reprinted from A Bonanni 2007 <i>Semicond. Sci. Technol.</i> 22 R41 DOI: https://doi.org/10.1088/0268-1242/22/9/R01 © IOP Publishing. With Permission. All rights reserved
1.13b	[79]	Licence n. 4532040888170 Reprinted from A Bonanni 2007 <i>Semicond. Sci. Technol.</i> 22 R41 DOI: https://doi.org/10.1088/0268-1242/22/9/R01 © IOP Publishing. With Permission. All rights reserved
1.15	[101]	Licence n. 4454280987338 Reprinted from A. Georgakilas et al., “Nitride Semiconductors: Handbook on Materials and Devices”, chapter 3, (2006), with the permission of John Wiley and Sons Publishing.
1.16	[107]	Licence n. 4454290324364 Reprinted from H. Morkoç, “Handbook of Nitride Semiconductors and Devices: Materials Properties, Physics and Growth, Volume 1”, Chapter 3, (2009), with the permission of John Wiley and Sons Publishing.
1.19b	[9]	Licence n. 4454290545332 Reprinted from A survey of gallium nitride HEMT for RF and high power applications, <i>Superlattice. Microst.</i>, 109 (2017), pp. 519-537, A.S. Fletcher et al. Copyright (2017), with permission from Elsevier
1.20	[23]	Licence n. 4454291082511

		Reprinted Sten Heikman, Stacia Keller, Yuan Wu, et al, J. Appl. Phys., vol. 93, no. 12, p. 10114-10118, Jun 2003. with the permission of AIP Publishing
2.1	[123]	Permission granted w/o licence n.
2.2	[127]	Licence n. 4454300435772 Reprinted from M A Moram and M E Vickers 2009 <i>Rep. Prog. Phys.</i> 72 036502 DOI: https://doi.org/10.1088/0034-4885/72/3/036502 © IOP Publishing. With permission. All rights reserved
2.5	[129]	Licence n. 4454301349956 Reprinted by permission from Springer: Springer Nature, “Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 3 Scattering and diffraction” by D.B. Williams, C.B. Carter, (2009) Copyright. With permission of Springer Publishing
2.8	[130]	Licence n. 4454310444233 Reprinted from M.H. Wong, F. Wu, T.E. Mates, J.S. Speck, U.K. Mishra, J. Appl. Phys., 104 (2008), p. 093710. with the permission of AIP Publishing
2.10	[129]	Licence n. 4454310831924 Reprinted by permission from Springer: Springer Nature, “Transmission Electron Microscopy, A Textbook for Materials Science – Chapter 9 The instrument” by D.B. Williams, C.B. Carter, (2009) Copyright. With permission of Springer Publishing
2.12	[131]	Reprinted Figure with permission of the author.
2.16	[139]	Licence n. 4454320838240 Reprinted from Introductory Raman Spectroscopy – Chapter 1, Elsevier book., J. R. Ferraro, Kazuo Nakamoto, Chris W. Brown Copyright (2003), with permission from Elsevier
2.17	[141]	Licence n. 4454321353003 Reprinted from Hiroshi Harima 2002 <i>J. Phys.: Condens. Matter</i> 14 R967 DOI: https://doi.org/10.1088/0953-8984/14/38/201 © IOP Publishing. All rights reserved
2.19	[143]	Licence n. 4454330392507 Reprinted by permission from Springer: Springer Nature, “Electrical characterization of semiconductor materials and devices—review” – Deen, M.J. & Pascal, F. J Mater Sci: Mater Electron (2006) 17: 549, (2006) Copyright. With permission of Springer Publishing
2.20	[144]	Permission granted w/o licence n.
2.21	[144]	Permission granted w/o licence n.

Permissions to reproduce third party Tables:

Table	Reference	Licence n. – notes
1.1	[3]	Copyright (2006) The Japan Society of Applied Physics, DOI: https://doi.org/10.1143/JJAP.45.7565 .
1.2	[3]	Copyright (2006) The Japan Society of Applied Physics, DOI: https://doi.org/10.1143/JJAP.45.7565 .
1.3	[26]	Permission granted w/o licence n. Reproduced from Rinke et al. “Consistent set of band parameters for the group-III nitrides AlN, GaN, and In”, DOI: https://doi.org/10.1103/PhysRevB.77.075202 .
1.4	[43]	Permission granted w/o licence n. Reproduced with IEEE permission, © (2012) IEEE, DOI: https://doi.org/10.1109/SMElec.2012.6417246 .

Permission reproducing Figure from "Properties of GaN and related compounds studied by means of Raman scattering"

Pace, Simona

mer 14/11/2018 11:42

Posta inviata

A:harima@dj.kit.ac.jp <harima@dj.kit.ac.jp>;

14.11.2018

Dear Prof. Harima,

I am completing my PhD thesis at Imperial College London entitled "Characterisation of scandium- and iron-based GaN for high electron mobility transistors".

I seek your permission to reprint, in my thesis an extract from: "Properties of GaN and related compounds studied by means of Raman scattering". The extract to be reproduced is: Figure 2.

I would like to include the extract in my thesis which will be added to Spiral, Imperial's institutional repository <http://spiral.imperial.ac.uk/> and made available to the public under a CC BY-NC.

If you are happy to grant me all the permissions requested, please return a signed copy of this letter. If you wish to grant only some of the permissions requested, please list these and then sign.

Yours sincerely,

Simona Pace

Permission granted for the use requested above:

I confirm that I am the copyright holder of the extract above and hereby give permission to include it in your thesis which will be made available, via the internet, for non-commercial purposes under the terms of the user licence.

Signed:

Name:

Organisation:

Job title:

Permission reproducing Figure from "HREM study of stacking faults in GaN layers grown over sapphire substrate"

Pace, Simona

mer 14/11/2018 11:40

Posta inviata

A:ruterana@lermat8.ismra.fr <ruterana@lermat8.ismra.fr>;

14.11.2018

Dear Prof. Ruterana,

I am completing my PhD thesis at Imperial College London entitled "Characterisation of scandium- and iron-based GaN for high electron mobility transistors".

I seek your permission to reprint, in my thesis an extract from: "HREM study of stacking faults in GaN layers grown over sapphire substrate". The extract to be reproduced is: Figure 2.

I would like to include the extract in my thesis which will be added to Spiral, Imperial's institutional repository <http://spiral.imperial.ac.uk/> and made available to the public under a CC BY-NC.

If you are happy to grant me all the permissions requested, please return a signed copy of this letter. If you wish to grant only some of the permissions requested, please list these and then sign.

Yours sincerely,

Simona Pace

Permission granted for the use requested above:

I confirm that I am the copyright holder of the extract above and hereby give permission to include it in your thesis which will be made available, via the internet, for non-commercial purposes under the terms of the user licence.

Signed:

Name:

Organisation:

Job title: