# Defect Analysis of Aluminum Nitride

vorgelegt von

# **Tobias Schulz**

1. Staatsexamen Physik (Sek. II) aus Hanau am Main

von der Fakultät II - Mathematik und Naturwissenschaften der Technischen Universität Berlin zur Verleihung des akademischen Grades Doktor der Naturwissenschaften - Dr. rer. nat. -

genehmigte Dissertation.

Promotionsausschuss

Vorsitzender: Prof. Dr. M. Lehmann Berichter: Prof. Dr. A. Hoffmann Berichter: Prof. Dr. M. Kneissl Berichter: Prof. Dr. R. Fornari

Tag der wissenschaftlichen Aussprache: 17.05.2010

Berlin 2010 D 83

### Abstract

AlN ist ein vielversprechendes Materialsystem für optoelektronische Anwendungen im tiefen UV. Derzeit ist es jedoch nicht möglich, Material mit ausreichender n- bzw. p-Leitfähigkeit herzustellen. Die Ursachen hierfür sind jedoch weitesgehend nur in theoretischen, selten aber in experimentellen Untersuchungen behandelt worden. Dies ist vornehmlich darauf zurückzuführen, dass aufgrund der nicht ausreichenden Leitfähigkeit, viele etablierte Messverfahren, wie z.B. Deep-level-transient spectroscopy (DLTS) oder Hall-Effekt Messungen selten anwendbar sind.

In dieser Arbeit werden die n-Dotierung von AlN, sowie die wichtigsten Kompensationsmechanismen experimentell untersucht. Dafür stehen n-leitfähiges und semi-isolierendes Volumenmaterial, als auch epitaktisch gewachsene Schichten zur Verfügung. Um einen experimentellen Zugang zu den Störstellen in AlN zu erhalten, wird in dieser Arbeit, neben Lumineszenz- und Admittanzspektroskopie, vor allem die Thermolumineszenz (TL) genutzt. Die TL wurde hierbei erstmals für die Anwendung in einem Rasterelektronenmirkroskop konzipiert und aufgebaut. Dadurch wird eine ortsaufgelöste Analyse der Haftstellen im Bereich weniger  $\mu$ m erreicht. Mit dieser Methode konnten bisher nie gezeigte, nahezu vollständig isolierte TL Banden in AlN beobachtet werden, was eine exakte Bestimmung der Defektparameter erlaubt.

Die wesentlichen Ergebnisse unserer Untersuchungen lassen sich wie folgt zusammenfassen: Die n-Leitfähigkeit in den Volumenkristallen wird durch Si auf Al Platz hervorgerufen. Im Hinblick auf die widersprüchlichen Diskussionen in der Literatur finden wir keine Hinweise dafür, dass es sich bei diesem Defekt um ein metastabiles DX-Zentrum handelt. Vielmehr deuten unsere Ergebnisse auf einen stabilen Si Donator hin, der sich (je nach Konzentration) 110 - 150 meV unterhalb der Leitungsbandkante einbaut. Weiterführende Lumineszenzuntersuchungen zeigen Hinweise auf einen noch flacheren und daher möglicherweise geeigneteren Donator, etwa 60 - 80 meV unterhalb der Leitungsbandkante. Bezüglich der Kompensationsmechanismen sind Akzeptoren in der unteren und oberen Hälfte der verbotenen Zone identifiziert worden. In der unteren Hälfte der verbotenen Zone kommen wir, in guter Übereinstimmt mit ab-initio Rechnungen, zu dem Ergebnis, dass das wesentlichste Kompensationszentrum in n-leitfähigem AlN die Al Vakanz ist, welche als dreifacher Akzeptor wirkt. Es konnte gezeigt werden, dass eine Lumineszenzbande bei 3.3 eV mit der Al Vakanz direkt in Verbindung steht. Die Position dieses Defekts, welche bisher nur aus theoretischen Arbeiten bekannt war, liegt, im dreifach negativ geladenen Zustand, etwa 2 eV oberhalb der Valenzbandkante. Es konnte ferner gezeigt werden, dass die in der Literatur häufig wenig beachteten Akzeptoren in der oberen Hälfte der verbotenen Zone von elementarer Bedeutung für die Kompensation der n-Leitfähigkeit sind. Insgesamt wurden acht verschiedene akzeptorartige Haftstellen identifiziert, von denen drei, 520 meV, 625 meV und 860 meV unterhalb der Leitungsbandkante, in maßgeblicher Konzentration vorliegen und wesentlich die elektrischen Eigenschaften beeinflussen. So führen sie unter anderem zum Pinnen des Fermi-Niveaus, was die freie Ladungsträgerkonzentration bei Raumtemperatur wesentlich verringert. Diese drei Haftstellen wurden auch in epitaktischem AlN gefunden, was die grundsätzliche Bedeutung dieser Akzeptoren für die n-Dotierung von AlN unterstreicht. Die Elektronenhaftstelle, 520 meV unterhalb der Leitungsbandkante, besitzt zudem metastabile Eigenschaften, was direkt nachgewiesen werden konnte. Diese Haftstelle erzeugt die persistente Photoleitfähigkeit und wirkt außerdem als nichtstrahlendes Zentrum, was zu einem Abfall der Defektluminszenz mit steigender Temperatur führt. Dadurch werden erstmals die in der Literatur genannten niedrigen Aktivierungsenergien, die aus Lumineszenz Quenching Experimenten bestimmt wurden, erklärt.

### Abstract

AlN is a promising material system for optoelectronic applications in the deep UV. However, at present it is not possible to grow material with a sufficient n- or p-type conductivity. The reasons for this have mainly been treated in theoretical works, while experimental studies are lacking. Mainly, this is related to the fact, that well known characterization tools like deep level transient spectroscopy (DLTS) or Hall-effect measurements are barely applicable. In this work, n-type doping of AlN and the main compensation mechanisms are investigated experimentally. For our studies, n-type and semi-insulating bulk material, as well as various epitaxial AlN layers are available. For an experimental access to the defects, we will, next to luminescence and admittance spectroscopy, mainly use thermoluminescence (TL) measurements. In our novel approach, the TL was developed and established for the application in a scanning electron microscope, which enables spatially resolved defect analysis in the range of a few microns. With this method, we could record TL curves, showing almost completely isolated peaks, which have never been reported before. This allows a very accurate determination of the trap parameters.

The main results of out studies can be summarized as follows: The n-type conductivity in our bulk crystals is due to Si on Al site. With regard to to controversial discussion in literature, we find no evidence that this defect incorporates as a metastable DX center. Instead, we propose that it is a stable Si donor, incorporating about 110 - 150 meV below the conduction band (depending on the concentration). Indications for the presence of an even shallower and thus more favorable donor, incorporating about 60-80 meV below the conduction band, come from luminescence studies. Turning to the compensation mechanisms, acceptors in the lower and upper half of the bandgap have been identified. In the lower half of the bandgap, we find, in good agreement with ab-initio calculations, that Al vacancies are the main acceptors in n-type material, acting as triple acceptors. It could be shown that a luminescence band, peaking around 3.3 eV, is directly linked with the presence of this defect. The position of the Al vacancy, in the triply negatively charged state is 2 eV above the valence band, which has so far only been known from theoretical works. Furthermore, it could be shown that acceptors in the upper half of the bandgap are essential for n-type compensation of AlN, which have so far rarely been considered in literature. Eight acceptor-like traps have been identified, with three of them, i.e. 520 meV, 625 meV, 860 meV meV below the conduction band, occurring in substantial concentrations. These traps are strongly affecting the electrical properties of AlN due to Fermi-level pinning, which severely reduces the free electron concentration at room temperature. They have also been identified in epitaxial AlN, which underlines their principal importance for n-type doping of AlN. The electron trap, 520 meV below the conduction band shows metastable properties, which has, for the first time, experimentally been verified. This trap causes the persistent photoconductivity and acts as a non-radiative center, which causes a decrease of the defect-related luminescence with increasing temperature. This explains the low activation energies in literature, determined from luminescence quenching experiments, which have so far not been interpreted.

# Selbstständigkeitserklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit selbstständig verfasst habe und dass ich ausschließlich die angegebenen Quellen und Hilfmittel verwendet habe. Die Arbeit ist in gleicher oder ähnlicher Form noch keiner anderen Prüfungsbehörde vorgelegt worden.

Berlin, den

## List of publication

T. Schulz, K. Irmscher, M. Albrecht, C. Hartmann, J. Wollweber, R. Fornari, Phys. stat. sol. RRL, V. 1, p. 147 (2007)

K. Irmscher, T. Schulz, M. Albrecht, C. Hartmann, J. Wollweber and R. Fornari, Physica B: Condensed Matter, V. 401-402, p. 323 (2007)

H.-J. Rost, D. Siche, R. Müller, D. Gogova, T. Schulz, M. Albrecht, R. Fornari PSS(c), V. 4, p. 2219 - 2222 (2007)

T. Schulz, M. Albrecht, K. Irmscher, C. Hartmann, J. Wollweber and R. Fornari, Journal of Appl. Phys, V. 104, p. 038710 (2008)

K. Irmscher, M. Albrecht, B. Heimbrodt, M. Naumann, T. Remmele, D. Schulz, T. Schulz, R. Fornari, PSS(c), V. 6, p. 2658 (2009)

## Manuscripts under review

T. Schulz, M. Albrecht, K. Irmscher, C. Hartmann, J. Wollweber and R. Fornari 'Ultraviolet Luminescence in AlN: Recombination Mechanism and Structural Origin'. Submitted to Journal of Appl. Phys. (2010)

# Danksagung

Ich möchte ganz herzlich bei allen bedanken, die mich bei der Anfertigung dieser Arbeit unterstützt haben.

Mein besonderer Dank gilt Dr. Martin Albrecht und Dr. Klaus Irmscher, die mir bei allen experimentellen und wissenschaftlichen Fragen stets zu Seite gestanden haben. Auch wenn wir (was Formulierugen angeht) nicht immer derselben Meinung waren, so haben die Diskussionen darüber doch viel Spaß gemacht.

Bedanken möchte ich mich auch bei Prof. Dr. Axel Hoffmann, der mir bei wissenschaftlichen Fragestellungen und bei der experimentellen Untersuchungen an der TU Berlin stets weitergeholfen hat.

Prof. Dr. Roberto Fornari danke ich für die Möglichkeit der Promotion am Leibniz-Institut für Kristallzüchtung, Korrekturen an diese Arbeit, sowie für das Abfassen des Berichts.

Prof. Dr. Michael Kneissl danke ich für die Übernahme des Berichts.

Dr. Jürgen Wollweber und Carsten Harmann möchte ich für die AlN Proben und den elementaren Diskussion in den Kaffeepausen danken.

Einen Dank auch an Kerstin Banse für die Präparation von diversen Proben.

Dr. Vivian Kral, Carolin Schächterle, Dr. Maike Schröder und Andrea Lepper danke ich für das Korrigieren von Rechtschreibfehlern.

Bedanken möchte ich auch meinen Eltern, die mich mindestens einmal im Monat angerufen haben, um sich nach dem Stand meiner Promotion zu erkundigen.

# Contents

•	Abs	tract -	Deutsch	iii
•	Abs	tract		iv
•	List	of pub	lication	vi
•	Dan	ksagun	Ig	vii
1.	Intro	oductio	n	1
	1.1.	Dopin	g of AlN	1
	1.2.	Outlin	e of this work	3
1.	The	oretica	l background	5
	1.1.	Crysta	al Defects	5
		1.1.1.	Effective-mass states	5
		1.1.2.	Deep centers	7
	1.2.	Radia	tive transitions	9
		1.2.1.	Free excitons	9
		1.2.2.	Bound excitons	10
		1.2.3.	Electron-phonon coupling	10
		1.2.4.	Free to bound transitions	15
		1.2.5.	Donor-acceptor pair recombination	15
2.	Met	hods fo	or trap characterization	19
	2.1.	Therm	noluminescence / Thermally stimulated conductivity	19
		2.1.1.	Electron beam excitation	21
		2.1.2.	Thermoluminescence / Thermally stimulated conductivity $\ldots$ .	25
		2.1.3.	Curve fitting	27
		2.1.4.	Limitations of thermoluminescence measurements $\ . \ . \ . \ .$ .	27
		2.1.5.	Exemplifications	28
	2.2.	Admit	tance spectroscopy	36
		2.2.1.	Conventional admittance spectroscopy $\ldots \ldots \ldots \ldots \ldots$	37
		2.2.2.	Admittance spectroscopy in the free carrier freezeout region $\ldots$	38

3.	Exp	eriment	tal	39
	3.1.	Therm	oluminescence	39
	3.2.	Admit	tance spectroscopy	40
	3.3.	Lumin	escence investigations	41
	3.4.	Sample	es	41
		3.4.1.	Bulk AlN crystals	41
		3.4.2.	Sample contacting	44
		3.4.3.	Epitaxial AlN	44
		3.4.4.	Irradiation experiments	44
4.	Rad	iative t	ransitions	45
	4.1.	Lumin	escence properties of bulk AlN	45
	4.2.	Near b	andedge luminescence	46
	4.3.	Discus	sion	47
	4.4.	Defect	related luminescence in the near UV region	50
		4.4.1.	General aspects of the NUV luminescence	50
		4.4.2.	Properties of the $VL_A$ luminescence	55
	4.5.	Discus	sion	58
		4.5.1.	Recombination mechanism	58
		4.5.2.	Chemical nature of the involved defects	62
		4.5.3.	Conclusions	64
5.	Dop	ants an	nd traps	65
	5.1.	Therm	oluminescence	65
		5.1.1.	Bulk AlN crystals	65
		5.1.2.	Epitaxial AlN	72
	5.2.	Trap t	ype analysis	75
		5.2.1.	Electron paramagnetic resonance	75
		5.2.2.	Electron traps in bulk AlN	76
		5.2.3.	Spectrally resolved thermoluminescence	79
	5.3.	Discus	sion	80
		5.3.1.	Summary - trap parameters	80
	5.4.	Metast	table properties of traps	86
		5.4.1.	Persistent photoconductivity	86
		5.4.2.	Temperature dependent TL yield	87
		5.4.3.	Competitive non-radiative recombination	88
	5.5.	Discus	sion	90

	5.6.	n-type	conductivity and compensation mechanisms	95
		5.6.1.	Discussion	96
6.	Sum	nmary		101
Α.	Арр	endix		103
	A.1.	Therm	oluminescence curve analysis	103
		A.1.1.	Numerical curve fitting	103

# **List of Figures**

1.1.	Configuration coordinate diagram of a metastable DX center	8
1.2.	Configuration coordinate model depicting the electron-phonon coupling of	
	a deep center	11
1.3.	Schematic representation of the absorption and emission spectrum for a	
	defect with strong electron-phonon coupling	12
1.4.	Calculated envelope function of an luminescence band, using $S = 6$ for	
	several temperatures.	14
1.5.	Configuration coordinate diagram depicting the influence of small and	
	large electron-phonon coupling on the shape of the emission band	14
2.1.	Charge carrier statistics involving two defect states within the bandgap	20
2.2.	Simple model for the excitation process using above bandgap excitation.	21
2.3.	Generation rate per volume of e-h pairs caused by an electron beam of	
	20 keV with a beam current of 1 nA. $\ldots$	23
2.4.	Time dependence of the trap filling using an electron beam for excitation.	24
2.5.	Sketch for the TL/TSC emission due to heating the sample	26
2.6.	SEM image of a PVT AlN bulk crystal	29
2.7.	Spatially resolved TL, recorded in different regions	30
2.8.	TL curves, obtained from Region A after using different excitation densities.	30
2.9.	Cross sectional SEM of the epitaxial AlN specimen under investigation	31
2.10.	TL curves of the epitaxial AlN for different primary electron energies	31
2.11.	Spectrally resolved TL at 260 K (P1), showing two prominent radiative	
	channels at 690 and 410 nm	32
2.12.	Monte Carlo Simulation of the penetration depth for 15 keV and 30 keV $$	
	primary electrons. (The illustration shows a projection.)	33
2.13.	Peak intensity dependence of P1 and P2 with the primary electron energy.	
	The figure also shows the calculated generation rates in the uppermost $AlN$	
	layer	34
2.14.	TL model including electron and hole traps	35
2.15.	Spectrally resolved TL of an AlN bulk crystal	36
2.16.	Schottky barrier with applied ac-voltage under (a) reverse bias and (b)	
	forward bias	37
2.17.	Equivalent circuit for admittance spectroscopy measurements	38

3.1.	Sketch of the thermoluminescence (thermally stimulated conductivity) setup.	39
3.2.	Setup for the TL / TSC measurements	40
3.3.	Linear heating ramp, recorded by RhFe thermocouple and the PT100	
	sensor. The heating rate is $0.1 \text{ K/s.}$	40
3.4.	Sketch of the growth setup.	42
3.5.	(a) Spontaneously nucleated AlN boule after 24h of growth on a TaC lid.	
	(b) Single crystalline AlN, grown on a 4H SiC wafer	43
4.1.	(a) CL spectrum of an AlN bulk crystal showing luminescence bands in	
	the NUV and the VIS region. (b) PL spectrum of an AlN bulk crystal.	
	showing intense excitonic lines around 6 eV, as well as deep, defect related	
	luminescence bands.	45
4.2.	Fitted PL spectrum in the NBE region using four Lorentz curves. Next	
	to the most intense lines, i.e. $NBE_1$ and $NBE_2$ , weak transition can be	
	assumed at 6.028 eV (FX <sub>A</sub> ) and 5.998 eV (NBE <sub>3</sub> ). Additionally, minor	
	transitions are observed at lower energies ( $NBE_4$ - $NBE_7$ )	46
4.3.	CL spectra of an n-type and insulating AlN bulk crystal. The NUV region	
	of crystal (3) has been deconvoluted using two Gauss curves, centered at	
	3.32 eV VL <sub>A</sub> and 3.65 eV VL <sub>B</sub> . The FWHM for both curves is 560 meV.	50
4.4.	Normalized absorption spectra of an n-type and an insulating AlN crystal.	51
4.5.	Monochromatic CL images at 2 eV (a), 2.5 eV (b) and 3.5 eV (c) of the	
	300 keV electron irradiated area of an insulating AlN bulk crystal	52
4.6.	CL spectra of the electron irradiated and the untreated region of an in-	
	sulating bulk AlN. The NUV luminescence band has been fitted by two	
	Gauss curves, centered at 3.32 eV (VL <sub>A</sub> ) and 3.65 eV (VL <sub>B</sub> ). The FWHM	
	of both curves is 560 meV. $\ldots$	52
4.7.	Monochromatic CL at 3.5 eV of epitaxial AlN, irradiated by 300 keV elec-	
	trons	53
4.8.	CL spectra of the electron irradiated and the untreated region of epitaxial	
	AlN	54
4.9.	CL spectra of two nominally identical AlN boules	55
4.10	. Integrated intensity of the $\mathrm{VL}_\mathrm{A}$ band with excitation density. The slope	
	reveals a sub-linear dependence	55
4.11	. CL of the VL <sub>A</sub> at for beam currents of $I_{\text{Beam}} = 30$ nA and $I_{\text{Beam}} = 60$ pA	
	at (a) 7 K, (b) 350 K and (c) 450 K, respectively. $\ldots$	56
4.12	. Position of the $VL_A$ peak with excitation density at 7 K	56
4.13	. Shift of the $VL_A$ peak position (black solid line). The fit will be discussed	
	in section 4.5 $\ldots$	57

4.14. 4.15.	Temperature dependence of the VL <sub>A</sub> FWHM	57 60
5.1.	TL curves of AlN bulk crystals grown in the presence (absence) of SiC	
5.2.	inside the crucible	65
5.3.	a FWHM of 63 meV	66
	grown in the presence of SiC. The fit shows the isolated TL peaks (dotted lines) and the composite signal (dashed line)	67
5.4.	TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks	01
	(dotted lines) and the composite curve (dashed line)	68
5.5.	TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks (dotted lines) and the composite curve (dashed line).	69
5.6.	TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks	
57	(dotted lines) and the composite curve (dashed line)	69
5.7.	peaks (dotted lines) and the composite curve (dashed line)	70
5.8.	Simultaneous TL / TSC measurement of a weakly n-type AlN (grown in	
	the presence of SiC).	71
5.9.	TSC curve of a weaky n-type AlN (grown in the presence of SiC). This	
	lamp for excitation.	72
5.10.	(a) Low temperature part of a TL curve from epitaxial AlN, grown by	
	MBE on a SiC substrate.	73
5.11.	Lower curve: TL of epitaxial AlN grown by MOCVD on a silicon substrate.	79
5 19	TL curve of a burk AIN crystal (grown in the presence of SiC).	73 74
0.12. 5.12	Isotropic FPR signal $(a - 1.000)$ in AlN-Si after prolonged illumination	(4
0.10.	$(\approx 500 \text{ nm})$ at low temperatures. The signal persists up to 60 K	75

5.14. Correlation between the decrease of the EPR signal with temperature and	
the TL peak $A_0$	6
5.15. Admittance spectroscopy measurement of an n-type AlN crystals, showing	
the frequency dependence of the capacitance (C) and the conductance	
$(G/\omega)$ with temperature	7
5.16. Admittance spectroscopy measurement of an n-type AlN crystals, showing	
the frequency dependence of the capacitance (C) and the conductance	
$(G/\omega)$ with temperature	8
5.17. Arrhenius plot of the $G/\omega$ peaks from Fig. 5.15	9
5.18. Arrhenius plot of the $G/\omega$ peaks from Fig. 5.16	'9
5.19. Spectrally resolved TL curve of n-type AlN	0
5.20. Estimation of the $O_N DX^-$ level throughout the entire $Al_x Ga_{x-1}N$ alloy.	
The decoupling from the CB occurs at $x = 0.4$	5
5.21. Expected position of the TL peak, related to $O_N$ in its deep $DX^{(-)}$ con-	
figuration.	55
5.22. Temperature dependence of the conductance before and after illumination	
with light of 514 nm and $\sim 800 \text{ nm}$	6
5.23. Various TL curves recorded after sample excitation at different temper-	
atures. The isolated TL peaks (dotted lines) were calculated by varying	
the parameters pursuant to Tab. 5.4	7
5.24. (a) CL spectrum showing the $VL_A$ and a VIS luminescence band. Both	
bands have been fitted by one Gauss curve, respectively. (b) Temperature	
dependence of the integrated $VL_A$ and VIS intensities	8
5.25. Temperature dependence of the integrated $VL_A$ luminescence intensity.	
The application of the simple thermal quenching formula in Eq. $(1.23)$	
reveals an 'activation energy' of 67 meV. $\ldots \ldots \ldots \ldots \ldots \ldots $ 8	9
5.26. (a) Temperature dependence of the integrated VIS luminescence intensity	
using different excitation densities, recorded with a bandpass filter cen-	
tered at $1.8 \text{ eV}$ . (b) Calculated temperature dependence of the radiative	
recombination channel 'R' as drafted in Fig. 5.28 by solving Eq. 5.3 9	0
5.27. Illustration for the increased TL yield of $A_2$ , at elevated sample excitation	
temperatures	1
5.28. Simplified luminescence quenching model used for the calculation 9	3
5.29. CV measurements of two different, weakly n-type bulk crystals, grown in	
different runs	5
5.30. Proposed model for the weak n-type conductivity in AlN bulk crystals. $.9$	17

5.31. Alternative model assuming a stable $Si_{Al}$ donor and an acceptor like trap in	
the upper half of the bandgap with a thermal capture barrier. (a) Thermal	
equilibrium at T $\sim$ 10 K. (b) Optical excitation at T $\sim$ 10 K causing	
photoexcitation and subsequent occupation of the $\mathrm{Si}_{\mathrm{Al}}$ donor band with	
electrons. (c) Thermal activation of the $Si_{Al}$ impurity band around 60 K.	
The thermal capture barrier of the traps prevents an instant recapture of	
the electrons. (d) Capture of the free carriers by the deep level 'T' for	
T > 120  K.	100
A.1. Calculated TL curves for different ratios of $c_n^T$ and $c_n^R$	103
A.2. Calculated TL curves for different ratios of $n^T/N^T$	104
A.3. Effect of the re-trapping factor b on the TL curve	105

# **List of Tables**

3.1.	Elemental analysis of the main contaminants, as determined by SIMS	43
3.2.	Elemental analysis of other impurities, as determined by ICPOES	43
4.1.	The table shows the peak energy, FWHM, amplitude and energy difference	
	to the free A exciton (FX <sub>A</sub> ) $\ldots$	47
4.2.	The table shows the peak energy, FWHM, amplitude and energy difference	
	to the free A exciton, as determined for bulk AlN. the values were taken	
	from Ref. [1]	48
4.3.	Localization energies and estimated activation energies, using Haynes rule	
	assuming $\alpha = 0.19$	49
4.4.	SIMS data of the oxygen, carbon and silicon concentrations in insulating	
	and conductive AlN crystal. Sample I and II have been grown in the	
	presence of SiC. Sample III has been grown free of SiC	51
5.1.	Defects determined by TL in bulk AlN	81
5.2.	Electron traps determined by admittance spectroscopy in n-type AlN	81
5.3.	Defect parameters determined by TL in epitaxial AlN crystals	81
5.4.	TL fit parameters.	87
5.5.	Parameters used for the calculation of the luminescence quenching	94

# 1. Introduction

Aluminumnitride has the largest direct band gap among all group III nitrides [2]. It is very stable and resistant to degradation under conditions of harsh environments like high electric currents, high temperature and intense light illumination. These properties make AlN an interesting material for optoelectronic devices, operating in the deep UV. At present, the main obstacle for the exploitation of such devices is related to the difficulties in achieving sufficient n- or p-type conductivity. While in 1999, Fara et al. even claimed that AlN is an 'undopable' material [3], nowadays, it is well known that it can be doped n-type with Si and p-type with Mg. Electron concentrations between  $10^{15}$  cm<sup>-3</sup> -  $10^{17}$  cm<sup>-3</sup> at room temperature have been reached [4,5], while hole concentrations are only in the order of  $10^{10}$  cm<sup>-3</sup> [6]. The progress in the field of doping already enabled the demonstration of LEDs, operating at 210 nm [6] with an external quantum efficiency of  $10^{-6}$  %. However, many aspects about doping and compensation mechanisms in AlN are experimentally poorly documented and thus not fully understood. The reason for the lack of more experimental data is related to the difficulties in obtaining conductive material, which makes well known characterization tools like e.g. deep level transient spectroscopy (DLTS) or Hall-effect measurements often inapplicable. Therefore, these issues will be a major task of this thesis. In our investigations, we will mainly focus on n-type doping.

# 1.1. Doping of AIN

In the following, we will briefly summarize the state-of-the-art knowledge concerning n-type doping of AlN, which have mainly been obtained by means of ab-initio and luminescence studies. Generally, two compensation mechanisms are believed to reduce the n-conductivity in wide-bandgap systems like AlN, which have been discussed in terms of the 'doping-limit rule' [7].

- (i) Instability of shallow donors.
- (ii) Compensation by intrinsic acceptors. (Self-compensation)

The first point refers to lattice relaxations, which turn shallow donors into deep levels, similar to donors AlGaAs [8,9]. Such relaxations are believed to occur for numerous impurities in AlN, whereby the so called DX transition is of major importance. DX centers occur in three charge states (+/0/-), with (-) referring to the stable ground

state. Due to the fact that the latter is an acceptor-like state, DX centers cause Fermilevel pinning, typically far below the conduction band. Therefore, such dopants are usually unsuitable for obtaining conductive material.

The second point concerns compensation by native defects, whose formation is promoted as the Fermi-level approaches the conduction band. The physical origin for this effect is related to the fact, that a considerable amount of energy is gained when electrons are transferred between a high Fermi-level and the defects electronic state, deep in the gap. Thus, particularly for wide bandgap materials, this is a very important mechanism.

In literature, some defects and impurities have been discussed in more detail, which shall be reviewed now. Today, Si is the only known n-type dopant for AlN. However, whether it is a stable shallow donor or undergoes a DX transition is currently under discussion. Several theoretical and some experimental works claim that Si on Al site Si<sub>Al</sub> is a DX center [10–14]. The still satisfactory free electron concentration of silicon doped AlN is explained by a comparatively low thermal activation energy of the acceptor-like Si DX<sup>-</sup> configuration. In contrast, other groups propose that Si remains a shallow, effective-mass donor in the entire  $Al_xGa_{x-1}N$  alloy [5,15–19]. Next the controversial discussion concerning its incorporation into the AlN lattice, the thermal activation energies for Si doped AlN reported in literature are widely scattered, ranging from 86 meV [20], 180 meV [18] up to 282 meV [21]. The origin for these inconsistencies remain unclear.

With no other dopant, one has so far succeeded in growing n-conductive AlN. However, indications for the presence of other shallow donors, aside from Si, come from various luminescence studies in the near bandedge region. These luminescence spectra, typically reveal multiple bound excitons with low localization energies in the range of a few tenth meV [1,22,23,23–27,27–29], which suggests the presence of various shallow states. However, most of these reports focus on the position of the free excitons, while the none of these bound excitons has been attributed to a specific defect.

A hardly avoidable and highly soluble impurity in AlN is O on N site ( $O_N$ ). Several ab-initio studies [11, 12, 15, 16] and some experimental studies on  $Al_xGa_{x-1}N$  [19] consistently propose that this defect undergoes a DX transition. Due to the fact tat the  $DX^-$  state is far from the conduction band, O severely reduces the n-type doping efficiency due to Fermi-level pinning. For this reason, contamination of AlN with O needs to be prevented by all means. The properties of this important DX center have experimentally barely been investigated in AlN. Latest experimental results for O impurities have been published by Rosa and Tale in 1984, who determined a thermal activation energy of 600 meV from thermoluminescence measurements [30,31] using the fraction-glow technique [32]. However, their thermoluminescence curves suffer from a large amount of overlapping bands, which makes an attribution to one specific defect very difficult. Moreover, other reports reveal high resistances of oxygen doped AlN, suggesting considerably larger thermal activation energies than 600 meV [33].

With respect to self-compensation centers, Al-vacancies are believed to play an important role in n-conductive AlN. Their formation energy of this triple acceptors reaches negative values, as the Fermi-level approaches the conduction band [3, 11, 16, 34-38]. However, experimental data on Al vacancies are rare and important parameters, such as its position within the bandgap, are unknown. Some experimental results in this field come from luminescence studies in the defect related region. In the works of Nam et al. and Nepal et al., a luminescence band at 3.4 eV has been attributed to a donor-acceptor pair recombination, involving a shallow donor and isolated Al vacancies [39, 40]. However, this attribution is mainly based on conclusions by analogy to the yellow luminescence in GaN, while direct evidence is missing. Furthermore, the origin of luminescence bands in the region between 3 - 4 eV is discussed controversially in literature. For example, Dadgar [41] et al. and more recently Bastek [42] et al. attributed luminescence bands around 3.3 eV and 3.8 eV to be related to oxygen and silicon impurities, respectively. Partly, this is due to the fact that AlN typically exhibits various, strongly overlapping bands [41, 43–48] in this spectral range, which makes distinctive attributions very difficult. Thus, the involvement of Al vacancies in the defect related luminescence of AlN needs further experimental evidence.

# 1.2. Outline of this work

In this thesis, n-type doping and compensation centers are investigated in AlN by means of luminescence, thermoluminescence and admittance spectroscopy. Our studies have been carried out on bulk and epitaxial AlN. In a novel approach, the TL was developed and established for the application in a scanning electron microscope. This enables spatially resolved trap characterization in the range of a few microns. The theoretical and methodical aspects this method are discussed in chapter 2.

In chapter 4, the defects in n-conductive and semi-insulating AlN will be investigated by means of luminescence studies. Next to the near bandedge region, this also encloses the 'defect-related' luminescence region. Of particular interest will be the exploration of the influence of n-type doping. In chapter 5, we will investigate traps in n-conductive and semi-insulating AlN, mainly by means of thermoluminescence and admittance spectroscopy. We will determine trap parameters and, as far as possible, reflect upon their chemical nature. The most essential compensation centers and dopants in AlN will be discussed. In chapter 6, the major findings of this thesis are summarized.

# 1. Theoretical background

# 1.1. Crystal Defects

In the most general sense, a defect is any interruption of the crystals translation symmetry. Hereby, one distinguishes between (i) point defects, which involve single atoms (e.g. vacancies, substitutionals, interstitials) and (ii) extended defects, including rows or planes of atoms (e.g. dislocations, stacking faults).

Defects can modify the electrical properties of the host crystal by introducing energetic levels in the bandgap. From these states, electrons (holes) can be provided to the conduction (valence) band at much lower energies than it would take to overcome the bandgap. These electrically active defects are distinguished whether they contribute free electrons  $e^-$  or holes  $h^+$  to the host lattice. In case the ionization of a neutral defect is described by the reaction

$$D^0 \to D^+ + e^- \tag{1.1}$$

the defect is denoted as a single donor while

$$A^0 \to A^- + h^+ \tag{1.2}$$

characterizes a single acceptor state.

Donors and acceptors may coarsely categorized in 'effective-mass' and 'deep' centers. Effective-mass states are characterized by small energetic distances from the respective bandedge, typically in the order of a few tens of meV. Hence, a considerable amount of these donors (acceptors) are ionized at room temperature, contributing to the conductivity of the semiconductor. Therefore, the incorporation of effective-mass states is mandatory to obtain conductive material. In contrast, deep centers commonly introduce at much larger distances form from the respective bandedge, what makes them usually unsuitable for doping. A detailed mathematical analysis of the point defect theory is beyond the scope of this thesis. However, some basic properties of effective-mass and deep centers will though be outlined in the following sections.

## 1.1.1. Effective-mass states

Effective-mass defects introduce a weak disruption of the lattice periodic potential. As a consequence, the charged nucleus of a neutral effective-mass donor (acceptor) exerts only a weak potential on the excess charge carrier. For this reason, the electron (hole) wavefunction of effective-mass states is delocalized in space, This allows to introduce some major approximations to the mathematical description, which concern the motion of charge carriers in the semiconductor and the potential disruption created by the defect itself.

First, the motion of the electron (hole) is described in an analogous manner to that of a free particle in the vacuum [49,50]. The influence of the host lattice periodic potential is considered by substituting the electron (hole) mass by an effective-mass  $m^*$ . Assuming isotropic, nondegenerate and parabolic bands, the energy relation of a charge carrier is then simply given by

$$E \propto (\hbar/2m^*)k^2. \tag{1.3}$$

In analogy to Newtons second law, the electron mass  $m^*$  is proportional to  $(\frac{d^2E}{k^2})^{-1}$ . Since a delocalized wavefunction in real-space is represented by a localized wavefunction in momentum space (**k** space), the mathematical treatment only of effective-mass states only requires to consider a very small region of the parabola near **k**  $\approx$  0, as given by Eq. (1.3). For this reason, a constant effective electron (hole) mass is a good approximation for such defects. Typically, effective masses of electrons and holes are only a fractional amount of those in the vacuum.

Second, the effective-mass theory requires, that the potential U created by the defect nucleus, can be approximated by a single point charge in the form of

$$U(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r r} \tag{1.4}$$

Hereby, e is the electron charge, r the distance of the electron from the center and  $\epsilon_0$  ( $\epsilon_r$ ) the static dielectric constant of the vacuum (solid). Thus, the influence of the lattice periodic potential is approximated by the static dielectric constant of the semiconductor. Since  $\epsilon_r$  is a macroscopic quantity, this again requires that the wavefunction of the excess charge carrier is delocalized in space (in order to average over several lattice rows).

With the motion of a charge carrier, described by Eq. (1.3) in a potential in the form of Eq. (1.4), the mathematical treatment of a neutral, effective-mass donor (acceptor) becomes identical to that of a hydrogen atom, embedded in a dielectric medium. Therefore, the ionization energies of the donors or acceptors are much lower than the 13.6 eV for the hydrogen atom. This results in a discrete set of energetic levels of

$$E_n = \frac{e^4 m^*}{32\pi^2 \epsilon_0^2 \epsilon_r^2 \hbar^2} \cdot \frac{1}{n^2}$$
(1.5)

with an effective Bohr Radius of

$$a^* = \frac{4\pi\hbar^2\epsilon_0\epsilon_r}{m^*e^2} \tag{1.6}$$

Due to the simple potential in form of Eq. (1.4), the effective-mass model is independent of the particular chemical nature of the defect. In GaN, the calculated activation energies using effective-mass theory are in satisfactory agreement with the experimental data. Using,  $\epsilon_{\rm DC} = 9.5$ , [51] and  $m^* = 0.22m_0$  [52] in Eq. (1.5), effective-mass donors are expected to have ground state energies of ~ 33 meV. Such values have in fact been observed for effective mass donors in GaN, e.g.  $O_N$  (30.8 meV) or Si<sub>Ga</sub> (32.4 meV) [53]. For AlN it is not known whether there are any donors or acceptors, which may be described in accordance to the effective-mass theory. Using,  $\epsilon_{\rm DC} = 8$  [54] and  $m^* =$  $0.33m_0$  [55] in Eq. (1.5) suggests thermal activation energies around 70 meV.

#### 1.1.2. Deep centers

In contrast to effective-mass states, deep centers induce a strong disruption of the periodic lattice potential, The excess charge carrier is spatially highly localized near the center of the defect, which implies, that the mathematical description requires to consider a large region of **k**-space. The calculation is further complicated by the local defect potential, which is determined by the local atomic configuration in the vicinity of the defect. Since deep centers often cause a strong displacements of lattice atoms, this is a difficult task. Furthermore, due to a relaxation of the lattice, the defect potential may severely change when the electronic state of defect is altered. This effect is known as 'electron-phonon coupling', which also affects optical transitions, involving such defects.

#### **DX** centers

A special case of the deep defect is the so called DX-center. which has been studied for Si in AlGaAs alloys in most detail [9]. In literature, different models have been proposed, describing its electronic properties. In the following we will discuss the proposals by Lang et al. [56,57]. Their major observations were (i) a defect with a very small capture cross section at low temperatures (ii) persistent photo-conductivity (PPC) and (iii) very large differences between optical and thermal ionization energies. They attributed these properties to a metastable defect, which occurs in three charge states (+/0/-) within the bandgap. While the (+/0) states are shallow donor configurations, the negatively charged (acceptor like) state refers to the stable ground state. Thus, the neutral  $d^{(0)}$  state can lower its energy by capturing a second electron, forming a negatively charged DX<sup>-</sup> and a positively charged d<sup>+</sup> state. This formation reaction causes the full compensation of the shallow  $d^{(0)}$  levels with the Fermi-level, pinned at the DX<sup>-</sup> state. The formation reaction of a DX center is therefore given by [58]

$$2d^{(0)} \to d^{(+)} + DX^{(-)} \tag{1.7}$$

The macroscopic characteristics, which DX centers add to semiconductors, are illustrated best on the basis of a configuration coordinate diagram [59], as depicted in Fig. 1.1. Hereby, the ordinate is the total energy (vibronic + electronic energy) and the abscissa is a function of a general coordinate, which is an overall measure of spatial displacement of atoms in the vicinity of the defect.



Configuration coordinate

Figure 1.1.: Configuration coordinate diagram of a metastable DX center.

The parabola on the right-hand side, corresponds to the deep, negatively charged ground state of the DX center (DX<sup>-</sup>), while the two parabolas on the left hand side, depict the shallow configurations  $d^0$  and  $d^+$ . Due to a large lattice relaxation between both configurations, the potential minima of the parabolas strongly differ in their configuration coordinate.

According to the Franck-Condon principle, the electronic and the vibronic transition can be separated, due to the fact that the electronic transition occurs on a much shorter timescale [60]. In other words, the atoms cannot immediately respond to the electronic transition. Applied to our CC diagram, this means that photon excitation or recombination processes can only cause 'vertical' transitions. This explains the much larger optical excitation energies  $E_{\text{Opt}}$  of a DX centers compared to the thermal excitation energy  $E_{\text{Therm}}$ .

The PPC effect is initiated by the optical excitation of two electrons from the  $DX^-$  state into the conduction band. This results a large lattice relaxation from the DX into

the shallow configuration. The free electrons can be captured by the positively charged  $d^+$  states, which results in the neutrally charged, shallow  $d^0$  states. The entire photoexcitation process is given by

$$d^{+} + DX^{-} \xrightarrow{h\nu} 2e^{-} + 2d^{+} \longrightarrow 2d^{0}$$
(1.8)

Electrons form the shallow  $d^0$  state can now easily contribute to an increased conductivity of the semiconductor, since its thermal activation energy ( $E_D$ ) is small. At low temperatures, a thermal capture barrier for electrons  $E_B$  prevents the instant reconfiguration into the DX<sup>-</sup> state when the illumination is switched off. This causes the increased conductivity to persist. Thus, at low temperatures,  $d^0$  is a long-lived (metastable) state. However, at elevated temperatures, the thermal barrier  $E_B$  can be overcome and the defect reconfigures to the deep DX<sup>-</sup> state. Along with this transformation, the conductivity decreases.

## **1.2.** Radiative transitions

In the following sections, some of the basic radiative recombination mechanisms are briefly discussed.

#### 1.2.1. Free excitons

If the semiconductor possesses a very high degree of purity, above bandgap excitation causes free excitonic transitions. Due to the attractive forces between electron and holes, which is related to the Coulomb interaction, their motions is correlated. The resulting quasi-particle is known as an exciton. If the distance between the electron-hole pair is much larger than the lattice spacing, they are denoted as Wannier-Mott excitons. [49,61]. As for the effective-mass approximation, the motion of the electron hole pair is described as free particles in a vacuum, while the periodic potential of the lattice is considered by substituting the electron (hole) mass by an effective-mass  $m_e^*$  ( $m_h^*$ ). This makes the problem similar to a positronium, embedded in a medium with the dielectric constant  $\epsilon_r$ .

The photon energy  $E_{FX}$ , resulting from a radiative recombination energy of a free exciton is below the bandgap  $E_g$  of the semiconductor. Assuming isotropic, i.e.  $k = k_x = k_y = k_z$ , nondegenerate and parabolic bands, one obtains

$$E_{FX} = E_g + \frac{\hbar^2 k^2}{2(m_e^* + m_h^*)} - \frac{e^4 \mu^*}{32\pi^2 \epsilon_0^2 \epsilon_r^2 \hbar^2} \cdot \frac{1}{n^2}$$
(1.9)

The second term respects the kinetic energy of the exciton. The last term concerns the binding energy of the e-h pair due to the attractive Coulomb forces. Hereby, the parameter n depicts the excitation state of the free excitons with n = 1 as the ground state.

### 1.2.2. Bound excitons

The electron or the hole of an exciton can be bount to a point defect in the lattice. The recombination energy of such a bound exciton is given by

$$E_{BX} = E_g - \frac{e^4 \mu^*}{32\pi^2 \epsilon_0^2 \epsilon_r^2 \hbar^2} \cdot \frac{1}{n^2} - E_{\text{Loc}}$$
(1.10)

The last term in Eq. (1.10), denotes the localization energy of the exciton. The magnitude of the localization energy may provide information about the ionization energy of the underlying defect. Haynes found, that the localization energy of exciton complexes in Si scales linearly with the ionization energy of the defect it is bound to [62].

$$E_{Loc} = \alpha \cdot \mathbf{E}_T \tag{1.11}$$

Hereby,  $\alpha$  denotes a material specific parameter. Originally, Although, Haynes derived this relation for bound exciton complexes in silicon, it could be shown that this relation also holds for many other semiconductors. In GaN, Meyer et al. determined  $\alpha = 0.19$ for donor bound excitons [63]. Effective-mass donors in GaN typically have thermal activation energies around 30 meV, which implies localization energies are around 6 meV. This is in good agreement with experimental observations. For AlN, effective-mass donors are expected to have thermal activation energies of ~ 70 meV as described in section 1.1.1. Assuming that  $\alpha = 0.19$  also holds for AlN, this would imply slightly larger localization energies of ~ 13 meV.

## 1.2.3. Electron-phonon coupling

Radiative transitions in the defect related region may involve deep levels, whose local atomic configuration strongly depends on their electronic charge state. This effect is known as electron-phonon coupling and has important consequences for optical transitions, which we will discuss now. As for the DX centers, a useful concept for the qualitative understanding of this phenomenon is the configuration coordinate (CC) diagram, as displayed in Fig. 1.2. For exemplification, we assume identically shaped, parabolic bands, representing the defect in the ground  $\Psi^0$  and the excited state  $\Psi^*$ , with an electron in the conduction band. The lattice vibrations of each configuration, which are determined by the vibronic eigenstates of the harmonic oscillator, are indicated by the horizontal lines. Since we assume identical parabolas for  $\Psi^0$  and  $\Psi^*$ , the vibronic eigenstates have equidistant values, corresponding to one phonon energy of  $\hbar\omega$ . Noticeably, the potential minima of  $\Psi^0$  and  $\Psi^*$ , refer to different configuration coordinates, which is due to the fact that the excitation of electrons into the conduction band (from  $\Psi^0$ ) affects the spatial configuration of the atoms in the vicinity of the defect.





Figure 1.2.: Configuration coordinate model depicting the electron-phonon coupling of a deep center.

Starting from the vibronic ground state of  $\Psi^0$ , optical excitation of sufficient energy causes a 'vertical transition' into any excited vibronic state of  $\Psi^*$ . Hereby, the purely electronic absorption, which implies no vibronic interaction, is denoted as the zero-phonon line (ZPL), i.e.  $E_{\text{ZPL}}(0 \to 0)$ . This transition depicts the threshold energy, for the optical excitation of electrons from  $\Psi^0$ . Largely shifted parabolas however cause a very low overlap integral for the purely electronic transition, which is therefore barely observable. In our model, the largest transition probability, i.e. the resonance absorption, occurs for the transition from the ground state of  $\Psi^0$  into the 7th mode of the excited state  $\Psi^*$ , i.e.  $E_{\text{Ab}}(0 \to 7)$ . The absorption energy for this transition is given by

$$E_{\text{Res.}}(0 \to 7) = E_{\text{ZPL}} + (S - \frac{1}{2})\hbar\omega$$
 (1.12)

Hereby, S is a dimensionless parameter, denoted as the Huang Rhys factor, which depicts the average number of involved phonons [64]. Subsequent to excitation, the system quickly relaxes to the vibronic ground state of  $\Psi^*$ , which corresponds to a rearrangement of nuclei, assisted by phonon emission. In our model, the relaxation from n = 7 to n = 0 involves the emission of 7 phonons with the energy quanta of  $\hbar\omega$ . As the zero vibrational level of  $\Psi^*$  has been attained, radiative transitions may occur i.e. electron capture from the conduction band into  $\Psi^*$ . Likewise the absorption process, an arbitrary number of phonons can be involved with the largest transition probability at a photon energy of

$$E_{\text{Res.}}(0 \to 7) = E_{\text{ZPL}} - (S - \frac{1}{2})\hbar\omega.$$
 (1.13)

Obviously, the emission maximum occurs at lower energies than the absorption maximum, with the energy difference denoted as the Stokes shift  $\Delta E_S$ .

$$\Delta E_S = 2(S-1)\hbar\omega \tag{1.14}$$

Figure 1.3 shows a qualitative absorption and emission spectrum caused by a defect with a strong electron-phonon coupling. The spectrum consists of discrete phonon lines separated by the phonon energy  $\hbar\omega$  lines, as indicated in the figure.



Figure 1.3.: Schematic representation of the absorption and emission spectrum for a defect with strong electron-phonon coupling.

#### Huang Rhys model

Huang and Rhys developed a quantitative description for intensity distribution of radiative transitions involving defects with electron-phonon coupling [64]. During a radiative transition, the probability for the generation of a phonon is  $\pi_e = S(N+1)$ , while the probability for the absorption of a phonon is  $\pi_a = S \cdot N$ , with S as the Huang-Rhys factor and N as the Bose-Einstein statistic

$$N(T) = \frac{1}{\exp\left(\frac{\hbar\omega}{kT} - 1\right)} \tag{1.15}$$

Assuming that the probability for the emission of m and the absorption of n phonons is described by a Poisson statistic, i.e.

$$r_{mn} = \exp\left(-(\pi_e + \pi_a)\right) \frac{\pi_e^m \pi_a^n}{m! \ n!}$$
(1.16)

this leads to the transition matrix element

$$|M_{if}|^2 = |M_{eg}|^2 \exp\left(-S(2N+1)\right) \frac{(S(N+1)^m (S N)^n)}{m! n!}$$
(1.17)

with  $|M_{eg}|^2$  as the matrix element for the electronic transition. The intensity distribution of the phonon lines is then given by

$$I_{h\nu} = |M_{eg}|^2 \exp\left(-S(2N+1)\right) \left(\frac{N+1}{N}\right)^{\frac{\nu}{2}} I_p(2S\sqrt{N(N+1)})$$
(1.18)

with  $I_p$  as the modified Bessel function. Hereby, p denotes the total number of emitted phonons p = m - n with Negative p values, indicating the absorption of phonons. The calculated envelope function of an emission band, taking S = 6 and  $\hbar \omega = 100$  meV is depicted in Fig. 1.4 for several temperatures. Clearly, the ZPL is very low in intensity for such large Huang Rhys factors, while the peak is around p = 6.



Figure 1.4.: Calculated envelope function of an luminescence band, using S = 6 for several temperatures.

For luminescence bands, involving defects with a very strong electron-phonon coupling, the isolated phonon lines often merge into a broad band. In this case, only an unstructured envelope functions can be observed, which attains an almost Gaussian shape as e.g. described in Ref. [65]. The origin of this effect is depicted in Fig. 1.5.



Figure 1.5.: Configuration coordinate diagram depicting the influence of small and large electron-phonon coupling on the shape of the emission band.

From the ground state of  $\Psi^*$ , optical transitions can occur to any vibronic state of  $\Psi^0$ , as described above. For small *S* values ( $\Psi^0_A$ ), optical transitions occur in a region where parabola possesses a pronounced curvature. This results in an asymmetric shape of the emission band, with a steeper high energy side.

In contrast, radiative recombination involving strongly coupled defects with a large S factor ( $\Psi_{\rm B}^0$ ), causes optical transitions in a region where the gradient of the  $\Psi_{\rm B}^0$  parabola is approximately linear. As a result, the emission band attains a symmetrical, Gaussianlike shape. In the latter case, the full half maximum (FWHM) of the emission band ( $\Gamma_0$ ) at T = 0 is approximately given by

$$\Gamma_0 = \sqrt{8\ln(2)S} \cdot \hbar\omega \tag{1.19}$$

Increasing the temperature causes a characteristic broadening of luminescence bands. The physical origin for this effect is related to the increased transitions probability involving phonon absorption (p < 0) or emission of phonons (p >> S). According to Klick et al, the FWHM is governed by [66].

$$\Gamma(T) = \Gamma_0 \tanh\left(\frac{\hbar\omega}{2kT}\right)^{-1/2}.$$
(1.20)

Hence, monitoring the FWHM of an emission band with increasing the temperature allows to deduce the magnitude of the electron-phonon coupling.

### 1.2.4. Free to bound transitions

Free to bound transitions occur between a free electron (hole) and a hole (electron), localized at a defect site. Referring to the recombination of a free electron and a strongly localized hole, the emission energy is given by [67]:

$$E_{\rm eA} = E_{\rm g} - E_{\rm A} + E_k - \overbrace{p\hbar\omega}^{\rm e-h\ coupling}$$
(1.21)

Hereby,  $E_A$  is the thermal activation energy of the (deep) acceptor state and  $E_k$  the kinetic energy of the free electron. The last term refers to the electron-phonon coupling, whereby p determines the number of involved phonons of the discrete quanta  $\hbar\omega$ .

### 1.2.5. Donor-acceptor pair recombination

Semiconductors are often (partly) compensated and thus contain donors and acceptors. Optical transitions between these levels are denoted as donor-acceptor pair transitions (DAP). Considering above bandgap excitation, free electrons and holes subsequently become captured at ionized donor and acceptor sites, converting them to their neutral charge state. The photon energy, resulting from the subsequent recombination between a donor-acceptor pair is given by [67,68]

$$E_{\rm DAP} = E_{\rm g} - E_{\rm D} - E_{\rm A} + \underbrace{\overbrace{e^2}^{e^2}}_{4\pi\epsilon_0\epsilon_r r} - \underbrace{e^{-\rm h\ coupling}}_{p\hbar\omega}$$
(1.22)

Hereby  $E_{\rm D}$  ( $E_{\rm A}$ ) denotes the binding energy of the donor (acceptor) species. An important characteristic of DAP transitions is that they are influenced by Coulomb interactions between the charged donor and acceptor pair, subsequent to recombination. This corresponds to the fourth term in Eq. 1.22. This Coulomb-interaction increases the recombination energy, which is particularly pronounced for spatially close pairs. This term includes the dielectric constant of the material  $\epsilon_r$ , the spatial distance of the donoracceptor pair r, the elementary charge e and the dielectric constant of the vacuum  $\epsilon_0$ . As for Eq. 1.21, the last term in Eq. 1.22, denotes the number of emitted phonons p of the discrete quanta  $\hbar\omega$ .

The Coulomb interaction and the occupation dynamics add some characteristic features to DAP transitions, which facilitate their identification. At low excitation densities, the intensity of DAP recombinations exhibit a sublinear to linear dependence with increasing excitation density, as e.g. described in Ref. [69]. At high excitation densities, saturation occurs due to the fact that lifetimes and concentrations are finite. The saturation first affects of the distant donor acceptor pairs due to the fact that these pairs have a smaller overlap of the electron-hole wavefunctions and are thus slow recombining. Therefore, the fast recombining, spatially close pairs in contrast dominate the DAP transition under high excitation conditions. Due to the larger Coulomb interaction, these pairs are emitting at higher energies and the DAP band shows a characteristic blue shift as the excitation density increases. <sup>1</sup>

The temperature dependent intensity of DAPs may also provide information about the binding energies of the underlying defects. Increasing the temperature, causes the thermal emission rate of electrons (holes) from the donors (acceptors) into bands to increase. Hence, the intensity of the DAP quenches. These experiments allow to determine the thermal activation energy of the donor or acceptor, depending on which species is ionized

<sup>&</sup>lt;sup>1</sup>Similar blue shifts can be caused by screening of band potential fluctuation, as discussed e.g. in Ref. [70].

first. For the evaluation, a simple analytical expression may be used

$$I(T) = \frac{I_0}{\left[1 + A \cdot \exp(\frac{-E}{kT})\right]}$$
(1.23)

Hereby,  $I_0$  depicts the initial luminescence intensity, A the ratio of the probability for non radiative and radiative transitions, i.e.  $\frac{P_{\rm NR}}{P_{\rm R}}$  and E the thermal activation energy of the defect.<sup>2</sup>

<sup>&</sup>lt;sup>2</sup>High doping concentrations or strong compensation, can cause a breakdown of the standard DAP theory, as e.g. described in Reference [71].
## 2. Methods for trap characterization

In this section, we discuss the techniques, which we used to the characterization of traps in bulk AlN crystals. Since standard characterization tools like deep level transient spectroscopy or Hall effect measurements are often difficult to apply for AlN, we referred to alternative methods. This includes (i) TL measurements, which we developed for application in a scanning electron microscope. and (ii) admittance spectroscopy.

# 2.1. Thermoluminescence / Thermally stimulated conductivity

Thermoluminescence (TL) and thermally stimulated conductivity measurements (TSC) are a non-destructive, 'single shot' techniques for the characterization of trap levels. These methods are particularly useful for the characterization of highly insulating, widebandgap materials, like sapphire or AlN. Both methods rely on the same physics and the underlying models for the understanding are essentially identical. The basic idea of TL and TSC is to create a non-equilibrium condition by excitation of the semiconductor. For this purpose, typically optical sources or more rarely electron beams have been used. In our approach, we will use the electron beam of a scanning electron microscope, which allows combined cathodoluminescence and thermoluminescence measurements in one setup. After switching off the excitation source, electrons (holes) become captured at trap levels (recombination centers). Subsequently, by applying heat to the sample, the trapped electrons are released into the conduction band, which results in an increased conductivity (TSC) and the emission of luminescence (TL) by recombination with holes. Thus, recording the current or the emitted light light as a function of temperature results in a set of peaks, which provides information about the underlying electron traps. (The treatment for hole traps is analogous.) While TL is a purely optical method and no serious sample preparation is necessary, TSC measurements require electrical contacts on the sample.

In literature, a rather large amount of more or less complex models can be found, which describe the TL or TSC phenomena [72–74]. The differences are mainly related to the number of defects and their interactions, which are taken into account. All forthcoming considerations refer to the so called 'simple model of TL', which respects only two defects, i.e. one electron trap level 'T' and one recombination center 'R'. Figure 2.1 sketches the



simple model of TL, including some of the possible transitions with electrons and holes.

Figure 2.1.: Charge carrier statistics involving two defect states within the bandgap.

The mathematical treatment of all these transitions is principally possible but due to the large amount of unknown parameters often inappropriate. Thus, for the forthcoming descriptions, the dashed interactions in Fig. 2.1 will be disregarded, i.e.:

- i) The capture or emission of holes from the trap 'T', which restricts the interactions of the electron trap to the conduction band only. This is a good approximation for a wide bandgap material like AlN, where the distance of the trap level 'T' from the valence band is very large.
- ii) The thermal activation of electrons and holes from the recombination center 'R'. Recombination centers are typically midgap states, which implies that their distance from the bands in a wide bandgap material like AlN is rather large.
- iii) Direct transition between 'T' and 'R'. This point is a priori not warranted and has to be evaluated for each TL peak.

Hence, for all following descriptions, we will only take into account (i) electron capture into 'T' from the conduction band, (ii) electron emission from 'T' into the conduction band (iii) electron capture into 'R' from the conduction band and (iv) hole capture into 'R' from the valence band.

### 2.1.1. Electron beam excitation

Using an electron beam for sample excitation enables the creation of free electron-hole pairs in any semiconductor, independent of its bandgap as e.g. demonstrated in Reference [75, 76]. According to our 'simple model of thermoluminescence', Fig. 2.2 sketches the charge carrier dynamics for above bandgap excitation. The notation is in accordance with the Shockley-Read-Hall scheme [77,78]. Free e-h pairs are generated at a generation rate g. A fraction of electrons is prevented from recombination via 'R' due to trapping at 'T', causing a hole excess in the valence band. Hereby,  $c_n^T$  denotes the capture coefficient for electrons at 'T' and  $c_n^R$  ( $c_p^R$ ) the capture coefficient for electrons (holes) at 'R'. After 'T' has become saturated, the reduction of free carriers is solely via the recombination center 'R'. Since the excitation is carried out at low temperatures where thermal emission from the trap level does not play a role, the emission rate is set to zero, i.e.  $e_n^T = 0$ . The charge carrier dynamics for the excitation process are described by a set of coupled rate equations, as given in Eq.(2.1). The parameter, n(p) denotes the electron (hole) concentration in the conduction (valence) band;  $n^T (p^R)$  the electron concentration at the trap (hole concentration at the recombination center) and  $f^{\rm T}$  ( $f^{\rm R}$ ) the electron occupation ratio of the trap (recombination center). The derivations are identical to the ones of e.g. Chen et al. [79].



Figure 2.2.: Simple model for the excitation process using above bandgap excitation.

$$\frac{dn^T}{dt} = N^T c_n^T n(1 - f^T)$$
(2.1a)

$$\frac{dn}{dt} = g - N^T c_n^T n (1 - f^T) - N^R c_n^R n (1 - f^R)$$
(2.1b)

$$\frac{dp^R}{dt} = N^R \left[ c_p^R p f^R - c_n^R n (1 - f^R) \right]$$
(2.1c)

$$\frac{dp}{dt} = g + N^R c_p^R p f_R \tag{2.1d}$$

A convenient approach to estimate the efficiency of electron beam excitation for the occupation of traps (recombination centers) is by Monte Carlo (MC) simulations [80]. The following simulations have been carried out using the CASINO code <sup>1</sup>.

The MC simulation gives the energy dissipation per unit volume, which can then be used for the calculation of the e-h generation rate per unit volume via the expression

$$g = \frac{U}{e \cdot G_{e-h}} I_{\text{Beam}}$$

, where U represents the dissipated energy density in  $[eV/cm^{-3}]$  (obtained from the MC simulation),  $I_{\text{Beam}}$  the beam current and e the elementary charge.  $G_{e-h}$  denotes the effective average energy, which is necessary for the creation of an e-h pair. This threshold energy can be estimated using the expression of Ehrenberg and Gibbons [85]

$$G_{e-h} = 2.1 \cdot E_g + 1.3 \text{ eV}$$

, with  $E_g$  as the semiconductors bandgap. Figure 2.3 shows the spatial generation rate per unit volume<sup>2</sup>, depth integrated by 54 nm. The in plane resolution is  $(54 \times 39)$  nm<sup>2</sup>. The simulation was performed for primary electrons of 20 keV and a beam diameter of 2 nm using 10<sup>6</sup> electron trajectories and a beam current of I<sub>Beam</sub> = 1 nA.

The generation rate of e-h pairs per unit volume varies from  $g > 10^{25} \text{ s}^{-1} \text{ cm}^{-3}$ , close to the electron impact point to  $g \sim 10^{22} \text{ s}^{-1} \text{ cm}^{-3}$  at rim of the primary electron scattering volume. The penetration depth of the primary electrons is about 3  $\mu$ m and the widest lateral spreading diameter is around 5  $\mu$ m.

<sup>&</sup>lt;sup>1</sup>For the calculation, CASINO uses a modified continuous energy loss approximation by Joy and Luo [81], which is based on the model of Bethe [82]. For the cross-sections of each element, pre-calculated values are used from Ref. [83]. Details of the calculation can be found elsewhere e.g. Ref. [84]

<sup>&</sup>lt;sup>2</sup>The size of the unit volume determines the accuracy of the simulation. In the present case the volume of the unit cell is (54x54x39) nm<sup>3</sup>, which is about 0.00022 % of the entire scattering volume, which equals about 51  $\mu$ m<sup>3</sup>.



Figure 2.3.: Generation rate per volume of e-h pairs caused by an electron beam of 20 keV with a beam current of 1 nA.

Knowing the e-h pair generation rate, we can calculate the trap and recombination center occupation dynamics by solving Eqs. (2.1). For the calculation, we will use typical capture coefficients for traps and the recombination centers of  $c_n^T = 10^{-8} \text{ cm}^3 \text{s}^{-1}$ ,  $c_n^R = 10^{-10} \text{ cm}^3 \text{s}^{-1}$  and  $c_p^R = 10^{-10} \text{ cm}^3 \text{s}^{-1}$ . The trap and recombination center concentrations are taken to be  $N^T = 10^{18} \text{ cm}^{-3}$  and  $N^R = 10^{19} \text{ cm}^{-3}$ , respectively. The time dependence of the trap (recombination center) occupation ratio is displayed in Fig. 2.4 using generation rates of  $g = 10^{22} \text{ s}^{-1} \text{ cm}^{-3}$  ( $g = 10^{19} \text{ s}^{-1} \text{ cm}^{-3}$ ). The recombination center was assumed to be fully occupied with electrons, whereas the electron trap as completely empty. In the considered case, the trap and the recombination center have reached their maximum occupation level after about 0.1 ms for  $g = 10^{22} \text{ s}^{-1} \text{ cm}^{-3}$  and about 100 ms for  $g = 10^{19} \text{ s}^{-1} \text{ cm}^{-3}$ . Although the generation rates from the MC simulations must be as rough estimations, we can still conclude, that electron beam exposure times below one second are sufficient to occup all traps and recombination centers within the entire primary electron scattering volume. Thus, an electron beam for excitation of TL can be regarded as a very efficient source.



Figure 2.4.: Time dependence of the trap filling using an electron beam for excitation.

#### Spatial resolution of thermoluminescence measurement

The easy adjustable beam parameters in a SEM allows to perform TL measurements with a high spatial resolution in the range of a few microns. The principal idea of a spatially resolved TL analysis is to excite the specimen locally by confining the scanning area and subsequently detect the integrated TL signal. Self evidently, the resulting TL curve only contains information about the defects within the previously excited volume, i.e. the TL probe volume. This is particularly useful in case the sample under investigation has a spatially inhomogeneous distribution of traps and recombination centers. In such a case, decreasing the TL probe volume can reduce the number of TL peaks and thus simplify the interpretation of the TL curve, as will be demonstrated in section 2.1.5.

If the scanning area is much larger than the lateral spread of the scattered primary electrons, the TL probe volume is approximately given by the scanning area of the electron beam times the penetration depth of the electrons. However, this must not necessarily be the case due to secondary excitation effects. Hereby, two effect are crucial: (i) intense CL and (ii) charge carrier diffusion. Both effects can impair the spatial resolution of the TL measurement. An approximate expression of the effective diffusion length respecting both effects has been developed by Martinez [86].

$$L_{eff}^{2} = \frac{\tau}{1-\eta} \left( \begin{array}{c} Carrier diffusion \\ D \end{array} + \begin{array}{c} \begin{array}{c} Photoionization \\ \hline \eta \\ 3\alpha^{2}\tau \end{array} \right)$$
(2.2)

Hereby,  $\tau$  represents the minority carrier lifetime,  $\eta$  the radiative quantum efficiency, D the diffusion coefficient and  $\alpha$  the optical absorption coefficient. The first term is related to the diffusion of minority carriers, whereas the second term considers the photoexcitation. Since carrier lifetimes are very short in direct bandgap materials like AlN or GaN, the first term in Eq.(2.2) can be disregarded for such materials. In contrast, highly luminescent materials with large  $\eta$ , give rise to the second term. For instance, AlN is typically emitting bandgap, as well as defect related sub-bandgap luminescence. Particularly the long-wave defect luminescence has a small absorption coefficient  $\alpha$ , typically in the range of a few  $\rm cm^{-1}$ . Thus, the enlargement of the defect occupation volume due to photo ionization is expected to be pronounced, enlarging the TL probe volume. Such self absorption effects of intense luminescence have also been observed in TL investigations using optical excitation in the semiconductor SiC [87]. One has to keep in mind that Eq.(2.2) tends to overestimate the influence of photoexcitation on the TL probe volume. This is related to the fact, that sub-bandgap photoexcitation can be considered as a rather inefficient for the population of traps, which makes prolonged exposure times necessary. Since the electron beam excitation provides a very efficient source, short excitation times are sufficient for the trap population. Additionally, strong CL can be reduced by decreasing the beam current. Thus, small beam currents and short excitation times in the range of seconds are suitable settings for a spatial resolution, mainly given by the primary beam excitation volume.

#### 2.1.2. Thermoluminescence / Thermally stimulated conductivity

After the occupation of traps and recombination centers with charge carriers, the excitation source is switched off, while keeping T = const. While electrons are trapped at 'T', the free charge carriers in the bands diminish due to recombination via 'R'. When all free carriers have been depleted, the excess holes become located at the recombination center 'R'. Hence, the quasi Fermi level for electrons (holes) is now pinned to the trap (recombination) center, which represents the initial condition for the forthcoming TL/TSC measurement. In our simple model of thermoluminescence, the concentration of captured holes at the recombination center simply equals the concentration of captured electrons at the trap level for the reason of charge neutrality.

Figure 2.5 shows the charge carrier dynamics as the sample is heated. If the temperature

is sufficiently high, the electrons are released from the trap level 'T' into the conduction band. If the emitted electrons recombine with a hole, trapped at 'R', light is emitted, which is detected as TL. Additionally, the emitted electrons cause an increased conductivity, which can be detected as TSC. Therefore, TL curves consist of the trap and the recombination center characteristics, while TSC directly verifies the emission of charge carriers into the bands.





Figure 2.5.: Sketch for the TL/TSC emission due to heating the sample.

These processes can be described by means of the rate equation set given in Eqs.(2.3) which is identical to the one derived by e.g. Halperin and Braner [88]. Hereby n denotes the electron concentration in the conduction band,  $n^T (p^R)$  the electron concentration at the trap (hole concentration at the recombination center).

$$\frac{dn^T}{dt} = N^T \left[ c_n^T n(1 - f^T) - e_n^T f^T \right]$$
(2.3a)

$$\frac{dn}{dt} = N^T \left[ e_n^T f^T - c_n^T n (1 - f^T) \right] - N^R c_n^R n (1 - f^R)$$
(2.3b)

$$\frac{dp^R}{dt} = -N^R c_n^R n(1 - f^R) \tag{2.3c}$$

The thermal emission rate  $e_n^T$  in Eqs.(2.3) is given by

$$e_n^T = \frac{\overbrace{c_n^T}^s}{g} N_c \exp(-\frac{E}{kT})$$
(2.4)

For simplicity, the pre-factor  $\frac{c_n^T}{g}N_c$  is usually substituted with a temperature independent frequency factor s. The TL is proportional to the negative time derivate of the concen-

tration of holes, located at the recombination center 'R', i.e.  $TL \propto -\frac{d_p^R}{dt}$ , whereas the TSC is proportional to the concentration of electrons in the CB, i.e.  $I_{\text{TSC}} \propto n$ . Above a certain temperature, the semiconductor reattains thermal equilibrium and TL or TSC is no longer observed.

## 2.1.3. Curve fitting

The analysis of TL/TSC curves reveals thermal activation energies and frequency factors of the underlying defects. In literature, various methods have been presented, which may roughly be divided into: (i) Full TL curve reproduction and (ii) evaluation of distinct points of TL peaks (maxima, half-width, etc.). In this thesis, we will only refer to methods of the first kind. For the determination of trap parameters, we will use numerical fitting, which directly evaluates Eq. 2.3, as well as analytical fitting.

Numerical curve fitting has two advantages: It gives the most precise results and uses only true 'physical' parameters. Drawbacks are the tedious computational efforts, especially if the TL curves contain a large amount of overlapping peaks. Analytical solutions are much more easy to handle, particularly if the TL curves contain a large amount of superimposing peaks. However, this method requires some further approximations to Eq. (2.3), which is, in its present form, analytically not solvable. In this thesis, we will use the 'general-order model' as proposed in Ref. [89].

$$I_{TL} = (n_0^{\rm T})^b s \exp\left(-\frac{E}{kT}\right) (N^{\rm T})^{(b-1)} \left[1 + \left((b-1)\frac{s''}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-\frac{o}{b-1}}$$
(2.5)

with  $n_0^{\rm T}/N^{\rm T}$  as the ratio of occupied to the total concentration of traps; s as the frequency factor; E as the thermal activation energy of the trap level; k as the Boltzmann constant and b as the 'retrapping parameter'. Details about the approximations and some calculated TL curves using the numerical and analytical approach can be found in the appendix A.1.

#### 2.1.4. Limitations of thermoluminescence measurements

Generally, TL and TSC measurements are difficult to interpret and some crucial aspects shall be mentioned.

• One severe problem with TL arises from the fact that this technique requires two defect states, i.e. the trap, which is actually under investigation, and a recombination center. Thus, the TL signal is always composed of the emission rate of the trap level and the capture coefficient of the recombination center. In case of e.g. the radiative channel quenches, the trap level is concealed.

- In a standard TL/TSC setup, electron and hole traps are principally indistinguishable. Only under certain conditions, spectrally resolved TL can provide some information in this field, as described in section 2.1.5.
- Since electrons and holes are created simultaneously during the excitation step, it is rather difficult to obtain a well defined occupation of the traps or recombination centers.
- The trap population may redistribute during the emission of the TL/TSC. This factor makes conclusions about the absolute concentration of the traps very questionable.
- TSC curves may be affected by the electrical properties of the contacts. This particularly accounts for highly insulating materials and may add peculiar features to the TSC curve caused by non-equilibrium carrier injection during the heating of the sample or surface currents.

## 2.1.5. Exemplifications

#### Spatially resolved TL

Using the electron beam of an SEM for excitation enables spatially resolved measurements in the range of a few microns. As discussed above, for AlN, the spatial resolution is mainly determined by the primary electron scattering volume and photo-excitation due to intense CL. In this section, we will demonstrate spatially resolved TL analysis for a bulk AlN crystal.

The PVT crystals under investigation are single crystalline on a scale of several millimeters. However, the trap distribution of the specimen is inhomogeneous on a spatially far lower scale, which becomes evident from the secondary electron (SEM) image, displayed in Fig. 2.6. The SEM image shows charging effects, indicating a high resistivity, as well as conductive regions on a scale of several hundred microns. This shows that the free carrier concentration is strongly fluctuating. In such a case, a spatially resolved TL analysis can be advantageous as the following results show.



Figure 2.6.: SEM image of a PVT AlN bulk crystal.

In Fig.2.7, TL measurements were taken out after exciting three different regions of the sample, using identical primary electron settings and excitation times (20 keV / 3.3 pA / 15 s). The lower TL curve was recorded after excitation region A, which is about (120 × 120)  $\mu$ m<sup>2</sup>, the middle curve after excitation of Region B, which is about (600 × 600)  $\mu$ m<sup>2</sup>. The upper curve was recorded after excitation of the whole specimen (2×2)mm<sup>2</sup>. Regions A and B are depicted on the SEM image in Fig. 2.6. Next to the two peaks at 170 K and 210 K, a new TL peak emerges peaking around 350 K as the probe volume increases, indicating that the TL peak at 350 K originates predominantly from the surrounding of region A. Hence, confining the TL probe volume to region A volume may reduce the total amount of TL peaks and therefore simplify the interpretation of the TL curve.

However, strong CL yield may enlarge the trap population volume. In Fig. 2.8, all TL curves were recorded after excitation of only region A, as drafted in 2.6. As expected, at low excitation densities only two peaks at 170 K and 210 K are observed. However, as the excitation density increases, the TL peak at 350 K emerges again in the TL curve. As we know from the preceding measurements, this TL signal does not originate from region A. Hence, the probe volume must have increased due to a secondary excitation process i.e. optical excitation by intense CL. Conclusively, by using low excitation densities and short excitation times, the TL probe volume for AlN is mainly determined by the scanning area of the beam.



Figure 2.7.: Spatially resolved TL, recorded in different regions.



Figure 2.8.: TL curves, obtained from Region A after using different excitation densities.

#### Depth resolved TL

In the following, the possibilities of depth resolved TL measurements will be demonstrated on a epitaxial AlN layer. A cross sectional SEM image of this sample is shown in Fig. 2.9. The topmost layer is an AlN layer of 400 nm thickness, followed by a 3.250  $\mu$ m thick GaN layer, grown on a sapphire substrate.



Figure 2.9.: Cross sectional SEM of the epitaxial AlN specimen under investigation.

Figure 2.10 shows several TL curves, recorded for different primary electron energies, which incite on the topmost AlN layer. For each TL curve, the beam current was kept fixed at  $I_{\text{Beam}} = 3.5$  pA for a duration of  $t_{\text{Exc.}} \approx 15$  s, using different beam energies from 5 keV to 30 keV.



Figure 2.10.: TL curves of the epitaxial AlN for different primary electron energies.

Using primary electrons of 5 keV to 10 keV, only one peak at  $\sim 290$  K (P2) is visible in the TL curve. Sample excitation with primary electrons of 15 keV to 30 keV leads to the appearance of a second peak at  $\sim 260$  K (P1), while P2 declines. The reason is that the two TL signals are emitted from different regions of the sample, depicting its depth profile. From 5 keV to 10 keV, the only contribution to the TL comes from the topmost AlN layer related to peak (P2). If the acceleration voltage is further increased, a second TL peak (P1) emerges in the TL curve. The origin of P1 can easily be verified identified by a spectrally resolved TL analysis, recorded at  $\sim 260$  K as displayed in Fig. 2.11. Sapphire thermoluminescence is known to be characterized by these two radiative recombination channels at 690 nm and 410 nm, as observed here [90]. The GaN layer does not emit any TL within this temperature region.



Figure 2.11.: Spectrally resolved TL at 260 K (P1), showing two prominent radiative channels at 690 and 410 nm.

A qualitative picture of the defect population volume is provided by MC simulations of the primary electron scattering volume. Figure 2.1.5 shows the projected energy dissipation of 15 keV and 30 keV primary electrons inside the investigated sample, which consists of a 400 nm AlN, a 3250 nm GaN layer and a quasi infinite sapphire substrate. At 15 keV, the primary electrons penetrate about 1  $\mu$ m into the GaN layer, which is still about 2.5  $\mu$ m away from the sapphire substrate. However, already under these conditions, a sapphire related TL peak appears in the curve. Hence, secondary processes must have caused a defect population in the substrate. Due to the long range of this secondary effect, only the photoexcitation, due to intense CL emitted from the GaN layer, comes into account. Using 30 keV primary electrons the penetration depth of the primary electrons is still too low in order to create e-h pairs directly in the substrate. However, the optical excitation of the sapphire is enhanced due to even more intense CL from the GaN, as well as due to the fact that the CL is generated closer to the substrate.



Figure 2.12.: Monte Carlo Simulation of the penetration depth for 15 keV and 30 keV primary electrons. (The illustration shows a projection.)

In the following, the optical excitation effects will be discriminated more quantitatively. The absolute TL yield of P1 (sapphire) and P2 (AlN) are displayed in 2.13 for different primary electron energies. The maximum AlN related TL peak P2 is attained at 7 keV and decreases, as the acceleration voltage is further increased. In contrast, the intensity of the sapphire related TL peak P1 increases constantly and shows no saturation for the respected primary electron energies. In addition, Fig. 2.13 displays the generation rates of e-h pairs due to scattered primary electrons created in the AlN layer. For the calculation, the beam current was taken taken to be  $I_{\text{Beam}} = 3.5$  pA, as in the experiment. The largest generation rate in the AlN layer is predicted for 7 keV, which is in good agreement with largest TL intensity of P2. Using electrons with energies higher than 7 keV, leads to a decreasing generation rate in the AlN layer, in coincidence with the decrease of the AlN related TL peak P2. Hence, up to 10 keV ( $I_{\text{Beam}} = 3.5$  pA,  $t_{\text{Exc.}} = 15$  s), the defect population mechanism in the specimen is nearly exclusively due to e-h pairs generated by the scattered primary electrons while optical excitation plays a minor role. At 15 keV, the e-h pair density in the GaN and thus the CL, has become

sufficiently large to cause photoexcitation of the sapphire substrate. The uppermost generation rate in the GaN layer for primary electrons of 30 keV, should lead to the highest CL intensity in the GaN and therefore maximize the optical excitation of the sapphire substrate. This is also in a qualitative agreement with the measurement.



Figure 2.13.: Peak intensity dependence of P1 and P2 with the primary electron energy. The figure also shows the calculated generation rates in the uppermost AlN layer.

In conclusion, TL in a SEM provides several advantages: In case the defect distribution of the sample under investigation is inhomogeneous, a reduction of probe volume may result in a smaller number of superimposing TL peaks. This facilitates the evaluation of the TL curve and improves the accuracy of the determined trap parameters. In addition, adequate TL spectra can be compared with CL or SEM analysis.

#### Spectrally resolved TL

In a conventional approach, the TL is recorded by means of a broadband detector, i.e. a photomultiplier tube (PMT). The resulting curve is then used for the determination of the defect parameters, i.e. activation energy, frequency factor. However, such measurements do not reveal any information about the nature of the radiative recombination channels, which are active during the TL emission. For this purpose, the emitted TL has to be dispersed in a monochromator and detected by a CCD camera. The resulting TL curve

then contains temperature as well as emission energy dispersive information. This may provide information about the radiative recombination center and underlying trap type. Thus, under certain preconditions, spectrally resolved TL information may assist for distinguishing between electron and hole traps.

In order to observe TL peaks, resulting from an electron trap  $T_n$  and a hole trap  $T_p$ , one has to consider (at least) two different recombination centers, where the respective other charge carrier is located. A sketch of this model, including electron and hole traps is drafted in Fig. 2.14. Thermally activated electrons may then recombine radiatively with a hole, located at ' $R_p$ ', while a thermally activated holes undergo a radiative recombination with an electron at ' $R_n$ '. Thus, the TL from electron and hole traps is emitted in different radiative channels. In case, ' $R_n$ ' and ' $R_p$ ' have different positions in the bandgap, which is a likely scenario, the TL is emitted at different spectral positions ( $\lambda_1, \lambda_2$ ). However, a distinctive identification of the trap type only by spectrally resolved TL is not possible.



Figure 2.14.: TL model including electron and hole traps.

Figure 2.15 shows a spectrally resolved TL measurement of an AlN bulk crystal. Since the sensitivity of the CCD is much lower as compared to the PMT detector, large beam currents in the order of 300 nA and primary electron energies of 20 keV are typically necessary for our bulk AlN crystal.



Figure 2.15.: Spectrally resolved TL of an AlN bulk crystal.

## 2.2. Admittance spectroscopy

If the sample under investigation possesses a certain electrical conductivity, stationary electrical measurements can be applied for the characterization of traps. In this thesis, we will use admittance spectroscopy for the determination of trap parameters. Admittance spectroscopy (AS) was introduced by Losee [91], as a supplement for DLTS measurement [92] in 1974. AS enables the characterization of deep, charge carrier traps by recording the frequency and temperature dependent capacitance (or conductance) of a Schottky diode. Admittance spectroscopy measurements are often much easier to interpret compared to TL or TSC, since this method is only sensitive to majority carrier traps. For an accurate measurement, two requirement have to be met: (i) The traps under investigation need to be below the Fermi level and (ii) the sample needs to possess a sufficiently high conductivity. This is usually accomplished by a introducing an adequate amount of shallow donors (acceptors), which are ionized in the temperature region where the measurement is carried out. Although this configuration is desirable, it is not mandatory. For example, Pautrat et al. showed, that it is still possible to use AS in the freeze out region of the free carriers [93]. Before discussing these particularities, a brief introduction of the conventional AS shall be given.

#### 2.2.1. Conventional admittance spectroscopy

Assuming the presence of a shallow donor 'SD' above and deep electron traps 'T' below the bulk Fermi level, the application of a small ac bias voltage, typically in the range of  $U_{AC} < 100$  mV, to a Schottky diode causes a periodically alteration of the depletion zone. A forward bias causes a reduction, a reverse bias an enlargement of the depletion zone, as indicated in Fig.2.16(a) and (b).



Figure 2.16.: Schottky barrier with applied ac-voltage under (a) reverse bias and (b) forward bias.

In the presence of deep centers 'T', the periodically altering Fermi level is sweeping throughput this deep trap level. In case the ac-frequency is sufficiently low, the traps may easily respond to the ac-frequency by capturing and emitting charge carriers. This maximizes the density of ionized centers and thus the capacitance of the depletion zone. In contrast, the application of a very high bias frequency, the traps may no longer be able to respond. This causes a decrease of the density of ionized centers within the depletion layer and therefore a reduction of the capacitance. The lower limit of the depletion zone capacitance is then defined by the ionized shallow donors 'SD'. Plotting the capacitance C vs. the angular frequency  $\omega$ , results in a step like function, whereas the conductance  $\frac{G}{\omega}$  vs.  $\omega$  generates Gauss-like peak functions. The inflection points of the C or the maximum of  $\frac{G}{\omega}$  yield an identical frequency  $\omega_T$ . The gradient of  $\omega_T$  with temperature reveals the thermal activation energy of the trap, whereas the intersection at  $\omega = 0$  yields the frequency  $\omega_0$ .  $\omega_0$  is connected with the emission rate of 'T' via

$$\omega_0 = \frac{2c_n N_c}{g} \exp(-\frac{E}{kT}) \tag{2.6}$$

Using the temperature independent frequency factor 's' from Eq.2.4 one obtains

$$s = \frac{\omega_0}{2}$$

#### 2.2.2. Admittance spectroscopy in the free carrier freezeout region

In case the conductivity of the sample is very low, AS may be difficult. The difficulties that may arise are illustrated in an equivalent circuit diagram admittance spectroscopy measurement, as drafted in Fig. 2.17. It consists of a parallel circuit including the sample capacitance C and conductance G with the resistance  $R_s$  in series.



Figure 2.17.: Equivalent circuit for admittance spectroscopy measurements.

The actually measured capacitance  $C_m$  and conductance  $G_m$  is given by:

$$C_m = \frac{C}{(1 + R_s G)^2 + (\omega R_s C)^2}$$
(2.7a)

$$G_m = \frac{G(1 + R_s G) + R_s (\omega R_s C)^2}{(1 + R_s G)^2 + (\omega R_s C)^2}$$
(2.7b)

In an accurate admittance measurement,  $C_m \approx C$  or  $G_m \approx G$ . As one can see from Eq. 2.7, this is warranted if the series resistance is negligible, i.e.  $R_s \approx 0$ . However, in some cases, the series resistance  $R_s$  may become large. In this case, the reliability of the measurements can be confirmed by checking whether the capacitance saturates in the low frequency limit. For  $\omega \to 0$ ,  $(\omega R_s C)^2$  becomes negligible and  $C_m$  exclusively depends on  $R_s G$ . In case the measured capacitance is strongly affected by  $R_s$ , the temperature dependence of the series resistance should prevent the saturation of the capacitance in the low frequency limit. In conclusion, if the capacitance is temperature independent in the low frequency limit, the measurement can be regarded as accurate. Another indicator for an accurate measurement is a linear dependence of  $\omega_T$  over several orders of magnitude. Strong deviations suggest inadequate results.

# 3. Experimental

## 3.1. Thermoluminescence

The thermoluminescence (TL) and thermally stimulated conductivity (TSC) measurements were carried out in a Zeiss DSM microscope, with an attached Gatan MonoCL-3 system. A scheme of the experimental setup is drafted in Fig. 3.1. The TL, which is collected by a parabolic mirror above the specimen, is detected by either a broadband photomultiplier (PMT) or spectrally resolved by a CCD. The TSC signal is detected by a Keithley 617s electrometer, operable down to atto amperes. The sample is contacted by a wiring pin on the sample surface, while the backside contact is achieved by silver epoxy. In order to avoid interferences with leakage currents, the sample is placed on an insulating glass plate. This setup allows to record the TL and the TSC signal simultaneously.

The temperature of the cooling stage is monitored by two independent detectors, i.e. a RhFe thermocouple and a PT100 sensor. The RhFe sensor is linked to the Oxford ITC503 temperature controller, which governs the power of the heating element. The PT100 is placed directly next to the sample and thus allows a more precise control of the sample temperature. The PT100 is read out by a resistance meter. All instruments are controlled via the IEEE interface using a PC.



Figure 3.1.: Sketch of the thermoluminescence (thermally stimulated conductivity) setup. The sample stage, operating with liquid helium, is displayed in Fig. 3.2. This stage

allows nearly linear temperature ramping between 20 K and 450 K using heating rates of 0.1 K/s. A typical heating ramp, recorded by both temperature sensors, is displayed in Fig. 3.3. The maximum deviation between the PT100 and the RhFe sensor is 10 K.



1.RhFe thermocouple 2.PT100 resistor 3.Sample 4.Heater 5.Thermoshield

Figure 3.2.: Setup for the TL / TSC measurements.



Figure 3.3.: Linear heating ramp, recorded by RhFe thermocouple and the PT100 sensor. The heating rate is 0.1 K/s.

## 3.2. Admittance spectroscopy

Admittance spectroscopy measurements were carried out in a cryostat, operating in the temperature range between 100 K and 700 K. The sample temperature is controlled

by a Lake shore 340 in conjunction with a PT100 sensor, placed next to the sample. The specimen is fixed on a sapphire plate, which ensures the electrical isolation from the cryostat housing. Contacting the sample is achieved by positioning a flexible, gold plated wiring pin on the Schottky contact. The backside contact was realized using silver epoxy. The capacitance was detected using a LCR meter (HP 4284A) measuring bridge. For the admittance measurements, the frequency is swept between 20 Hz and 1 MHz, while keeping the sample temperature constant.

The same setup could also be used alternatively for TSC measurements. In this case, the LCR meter was replaced by an ampere meter (Keithley 617s) and a nearly ohmic contact was evaporated instead of a Schottky diode. This setup allows the excitation of the sample by means of a Xe-lamp.

## 3.3. Luminescence investigations

The cathodoluminescence measurements were carried out in a Zeiss DSM microscope, with an attached Gatan MonoCL-3 system. The luminescence is collected by a parabolic mirror that can be moved above the specimen. The luminescence can be recorded panchromatic or dispersed, using either a 150 (Blaze wavelength: 500 nm) or a 2400 (Blaze wavelength: 300 nm) grating in a 300 mm spectrometer. The light detection is realized either by a UV-enhanced photomultiplier (PMT) or a CCD camera, which are both cooled down to  $-40^{\circ}$ C. The response of the PMT ranges from  $\approx 185 - 850$  nm with a peak sensitivity at 420 nm. The temperature can be adjusted between 7 K and 450 K using a He cooled stage with a Oxford ITC-503 controller.

The photoluminescence studies have been carried out using a 193 nm excimer-laser for excitation and a UV enhanced spectrometer for detection, equipped with a bialkali photomultiplier tube. The sample was placed in a bath cryostat which allows sample temperatures down to 2 K. In order to avoid high excitation effects, a strong focus of the laser beam was avoided.

## 3.4. Samples

#### 3.4.1. Bulk AIN crystals

The principal idea of PVT is to sublime the AlN source material in a crucible at temperatures around 2000°C. The atomic Al and N atoms in the gaseous phase are then transported to the cooler growth region by a vertical thermal gradient. There, the gas species can either be deposited epitaxially on a seed or nucleate spontaneously on the crucible lid. All bulk crystals were grown at the Leibniz-Institute for Crystal Growth <sup>1</sup>. The growth experiments were carried in a radio-frequency heated furnace (10 kHz, 30 kW). The crucible material is tantalum carbide (TaC). Susceptor and insulation were made from graphite and porous graphite felt, respectively. A sketch of the growth reactor is displayed in Fig. 3.4. The temperatures are controlled by two infrared pyrometers on the lid and the bottom of the crucible. The temperature gradient between upper source surface and growth interface is adjusted by changing the coil position. Initially, the AlN powder has to be purified, particularly in order to reduce the initial oxygen contamination of 1.5 wt%. This purification step is carried out in a in a high purity nitrogen (99.999 %) for a duration of 48h at 1900°C. The growth of the AlN boules is carried out in the temperature range of  $2000 - 2125^{\circ}$ C at nitrogen pressures of 600 - 900 mbar. The distance between the top of the sintered AlN source and the crucible lid (or the AlN seed) is typically 10 - 20 mm. Details of the growth are described in reference [94].



Figure 3.4.: Sketch of the growth setup.

<sup>&</sup>lt;sup>1</sup>Group members are J. Wollweber, C. Hartmann and A. Dittmar

#### **Recondensation of AIN**

The recondensation of AlN can either occur due to spontaneous nucleation, or seeded on SiC. Figure 3.5(a) shows a typical self-nucleated AlN boule after 24 h of growth. From such boules, single crystalline pieces can be cut.

The seeded growth on SiC results in single crystalline AlN with diameters up to 35 mm and thickness of about about 1 mm. An example of AlN, grown on 4H SiC, is displayed in Fig. 3.5(b).



Figure 3.5.: (a) Spontaneously nucleated AlN boule after 24h of growth on a TaC lid. (b) Single crystalline AlN, grown on a 4H SiC wafer.

The typical concentrations of the main contaminants in a spontaneously nucleated and seeded bulk AlN crystal are listed in Tab.3.1, as determined by secondary ion mass spectroscopy (SIMS). Noticeably, using SiC inside the crucible substantially increases the concentration of carbon and silicon, while the oxygen concentration is only slightly increased.

Element [× $10^{19}$ cm <sup>-3</sup> ]	Ο	С	Si
Spontaneous nucleation	0.1-0.9	0.1-0.3	-
Seeded on SiC	1-3	10-20	10-30

Table 3.1.: Elemental analysis of the main contaminants, as determined by SIMS.

The concentrations of other elements, which can be found in all AlN crystals are displayed in Tab. 3.2. These values were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

Element [× $10^{18}$ cm <sup>-3</sup> ]	Fe	Cu	Ni	Co	Mn	W	Zn	Ph
All crystals	2	1	0.2	0.05	0.04	0.09	0.3	0.1

Table 3.2.: Elemental analysis of other impurities, as determined by ICPOES.

## 3.4.2. Sample contacting

For the electrical measurements, Ohmic or Schottky-contacts were prepared by evaporation (Edwards FL400) using a mask with hole diameters of 0.6 mm and 1.1 mm. The contact diameter is far below the diameter of single crystalline areas of the bulk crystals. The Schottky contacts consist of a 15 nm layer of Ni. An after treatment was not needed. Ohmic contacts were deposited on a single crystalline pieces, prepared from the boule. A 20 nm thick layer of Ti was followed by a 100 nm thick Au layer. Subsequently, the samples were annealed in at 900°C in nitrogen ambient for a duration of about 1 minute.

## 3.4.3. Epitaxial AIN

A minor fraction of the presented investigations were carried out on epitaxial AlN, grown by metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). The growth temperatures in these samples usually is in the range of 900-1200 °C. The specimen have been provided by the group of

- i) H. Amano and coworkers. Department of Materials Science and Engineering, Meijo University, Nagoya, Japan. The AlN films were grown on 6H-SIC substrates by high temperature MOCVD.
- ii) A. Dadgar and coworkers. Otto-von-Guericke-Universität Magdeburg, Institut für Experimentelle Physik, Fakultät für Naturwissenschaften, Universitätsplatz 2, 39106 Magdeburg, Germany. The AlN films were grown on silicon (111) substrates by MOCVD.
- iii) E. Monroy and coworkers. CEA-CNRS group Nanophysique et Semiconducteurs, CEA-Grenoble, INAC/SP2M/NPSC, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France. The AlN films were grown on 6H-SiC substrates by molecular beam epitaxy (MBE).

## 3.4.4. Irradiation experiments

For radiation damage studies, AlN crystals have been exposed to 300 keV electrons in a Philips CM30 transmission electron microscope. The beam current of was about 1 nA for a duration of about 30 minutes. The beam was focused down to an area of about 20  $\mu$ m in diameter.

# 4. Radiative transitions

In this chapter, we will use luminescence investigations for the characterization of defects in AlN. This encloses the near bandedge, as well as the 'defect related' luminescence of AlN in the near UV region. Based on this data, we will discuss the nature of the involved defects and evaluate their position in the bandgap.

## 4.1. Luminescence properties of bulk AIN

The bulk AlN crystals exhibit a rich amount of luminescence bands between 1.5 eV and 6 eV. Due to the large bandwidth, it is not possible to record the entire spectral range with a single detection system. Thus, the spectrum in Fig. 4.1(b) has been recorded with an UV optimized photoluminescence (PL) setup, showing the spectral range between 3-6 eV and Fig. 4.1(a) displays the spectral region from 1.5 eV to 4.5 eV, recorded with the CL setup. Both spectra are grating and photomultiplier response corrected.

Several luminescence bands are observed, as indicated in the figures: (i) Luminescence in the near bandedge (NBE) region around 6 eV, which is the most intense transition between 3 - 6 eV, (ii) deep UV luminescence between 4 - 5 eV, (iii) near UV (NUV) between 3 - 4 eV and (iv) luminescence in the visible (VIS) range between 1.5 - 2.5 eV.



Figure 4.1.: (a) CL spectrum of an AlN bulk crystal showing luminescence bands in the NUV and the VIS region. (b) PL spectrum of an AlN bulk crystal, showing intense excitonic lines around 6 eV, as well as deep, defect related luminescence bands.

## 4.2. Near bandedge luminescence

First, we will investigate the intense near bandedge luminescence in more detail. A high resolution PL spectrum between 5.89 eV and 6.05 eV of an AlN bulk crystal (silicon doped) is displayed in Fig. 4.2. Multiple, overlapping lines are visible around 6 eV and four minor peaks between 5.98 eV and 5.9 eV. The spectral region around 6 eV has been fitted using four Lorentz curves. Very weak lines can be presumed at 6.028 eV (FX<sub>A</sub>) and 6.004 eV (NBE<sub>3</sub>), while strong lines are observed at 6.012 eV (NBE<sub>1</sub>), 6.006 eV (NBE<sub>2</sub>). The linewidths vary between 4 meV and 8 meV. Additionally, minor peaks are found at 5.963 eV, 5.917 eV, 5.907 eV and 5.903 eV (NBE<sub>4</sub>-NBE<sub>7</sub>), respectively. In Tab. 4.1, the peak energies and amplitudes of the all NBE transitions are summarized. The full width at half maxima (FWHM) are only given for the strongest lines.



Figure 4.2.: Fitted PL spectrum in the NBE region using four Lorentz curves. Next to the most intense lines, i.e.  $NBE_1$  and  $NBE_2$ , weak transition can be assumed at 6.028 eV (FX<sub>A</sub>) and 5.998 eV (NBE<sub>3</sub>). Additionally, minor transitions are observed at lower energies (NBE<sub>4</sub>-NBE<sub>7</sub>).

	Peak E (eV)	FWHM (meV)	Amplitude	$\Delta E_{\rm FX_A}$
$\mathrm{FX}_{\mathrm{A}}$	6.028	-	0.06	-
$NBE_1$	6.012	4	0.40	$16~{\rm meV}$
$NBE_2$	6.006	8	0.79	$22~{\rm meV}$
$NBE_3$	5.998	-	0.07	30  meV
$NBE_4$	5.963	-	0.04	65  meV
$NBE_5$	5.917	-	0.02	$111~{\rm meV}$
$NBE_6$	5.907	-	0.02	$121~{\rm meV}$
$\operatorname{NBE}_7$	5.903	-	0.04	$125~{\rm meV}$

Table 4.1.: The table shows the peak energy, FWHM, amplitude and energy difference to the free A exciton  $(FX_A)$ 

## 4.3. Discussion

The highest energetic transition in our bulk crystals is a small feature around  $E_{\rm FX_A} = 6.028$  eV, which might be related to the recombination of the free-A-exciton. Latest reports depict the position of the free-A exciton  $E_{\rm FX_A}$  to be between 6.023 eV [23] in homo-epitaxial and 6.036 - 6.05 eV [27, 29] in bulk AlN. The minor shifts of a few meV have been attributed to impurity concentration fluctuations. This is in reasonable agreement with our value. Hence, although poorly resolved in our spectrum, we will use  $E_{\rm FX_A} = 6.028$  eV for calculating the energetic difference of NBE<sub>1</sub>-NBE<sub>7</sub> from the free-A-exciton, which are summarized in Tab. 4.1.

The localization energies of NBE<sub>1</sub> to NBE<sub>3</sub>, range from 16 meV and 30 meV. This is within the range of typically reported binding energies for bound excitons in AlN, which are between 7 meV and 39 meV [1,22–26]. In Tab. 4.2, the parameters for the free-A and three bound excitons transitions are summarized, as taken form Ref. [1]. The values were determined for bulk crystals, grown by CrystalIS. Noticeably, the localization energies of NBE<sub>1</sub> and NBE<sub>2</sub> are in perfect agreement, which suggests that they refer to the same defects.

Possible assignment	Peak E (eV)	FWHM $(meV)$	Amplitude	$\Delta E_{\rm FX_A}$
FXA	6.026	-	0.06	-
?	6.019	7	0.46	$7 \mathrm{~meV}$
$NBE_1$	6.010	3.6	1.72	16  meV
NBE <sub>2</sub>	6.004	4.2	0.29	22  meV

Table 4.2.: The table shows the peak energy, FWHM, amplitude and energy difference to the free A exciton, as determined for bulk AlN. the values were taken from Ref. [1]

The minor peaks (NBE<sub>4</sub> and NBE<sub>5</sub>) have so far not been reported in literature. Possibly, they are also related to bound excitons. In this case, their localization energies are very large.

With regard to NBE<sub>6</sub> and NBE<sub>7</sub>, these transitions are related to phonon replicas. Adding a phonon energy of E = 104 meV, which is close to the longitudinal optical (LO) phonon energy of 110 meV (see in Ref. [95]), to their emission energies equals

$$E_{\text{NBE}_6} + 104 \text{ meV} = 6.011 \text{ eV}$$
 (4.1)  
and  
 $E_{\text{NBE}_7} + 104 \text{ meV} = 6.007 \text{ eV}.$  (4.2)

This is in good coincidence with the positions of  $NBE_1$  and  $NBE_2$ . Thus, we attribute  $NBE_6 / NBE_7$  to phonon replicas of  $NBE_1 / NBE_2$ , respectively. The similar intensity ratios of  $NBE_6/NBE_7$  and  $NBE_1/NBE_2$  further corroborate this assignment.

Whether the excitonic lines NBE<sub>1</sub>-NBE<sub>3</sub> are bound to donors or acceptors cannot be clarified at the moment. If we tentatively assign them to donor bound excitons, we can roughly estimate the thermal activation energy of the underlying donors by using Haynes rule, as described in section 1.2.2. Since there is no experimentally determined  $\alpha$  value for AlN, we will refer to  $\alpha = 0.19$ , as determined for donor bound excitons in GaN [63]. Presuming that this value is valid for AlN, the resulting thermal activation energies of the underlying donors are 80 meV, 120 meV and 160 meV, respectively, as summarized in Tab. 4.3.

Bound exciton	$\mathrm{E}_{\mathrm{Loc}}$	Donor activation energy
		$\alpha = 0.19$
$NBE_1$	$16~{\rm meV}$	$\approx 80 \text{ meV}$
$NBE_2$	$22~{\rm meV}$	$\approx 120 \text{ meV}$
$NBE_3$	$30~{\rm meV}$	$\approx 160 \text{ meV}$

Table 4.3.: Localization energies and estimated activation energies, using Haynes rule assuming  $\alpha = 0.19$ .

A thermal activation energy of 80 meV for the donor related to NBE<sub>1</sub> is in very good agreement with the estimated value for effective-mass donors in AlN (see section 1.1.1). More evidence for the presence of such a shallow donor will be given in the next sections. Therein, we will identify a donor with a thermal activation energy of about 60 - 80 meV from luminescence studies in the near UV region. Since this thermal activation energy is considerably lower than the values reported in literature for Si on Al site, this suggests that there are alternative and maybe even more suitable n-type dopant than Si. However, one has to keep in mind that such shallow donor states might refer to metastable defects, which are typically unsuitable for doping. Excitons, bound to such defects have also been suggested in GaN [96]. In chapter 5, we will show that Si introduces a donor state about 120 meV below the conduction band. This value is in good agreement with the underlying donor of NBE<sub>2</sub>, suggesting that this exciton might be related to Si donors.

## 4.4. Defect related luminescence in the near UV region

In the following, we will study the defect related luminescence of AlN. Hereby, we will characterize the underlying recombination mechanism and determine the positions of the involved defect within the bandgap. For determination of the influence of compensation centers, these studies are carried out on n-conductive and insulating material.

### 4.4.1. General aspects of the NUV luminescence

#### Influence of n-type doping

Figure 4.3 shows CL spectra of insulating (sample I and III) and a weakly n-type AlN crystals (sample II) for comparison. The insulating specimen (I, III) exclusively exhibit luminescence in the VIS range, while the NUV luminescence is almost absent. In contrast, the n-type crystal (sample II) exhibits a pronounced luminescence band in the NUV region, which dominates the defect related luminescence within this spectral range.



Figure 4.3.: CL spectra of an n-type and insulating AlN bulk crystal. The NUV region of crystal (3) has been deconvoluted using two Gauss curves, centered at  $3.32 \text{ eV VL}_A$  and  $3.65 \text{ eV VL}_B$ . The FWHM for both curves is 560 meV.

The impurity concentrations of these samples have been determined by secondary ion mass spectroscopy (SIMS), Sample I and II, which have been grown in the presence of SiC inside the crucible, both reveal similar concentrations of silicon, carbon and oxygen in the order of  $10^{19} - 10^{20}$  cm<sup>-3</sup>. Sample III, which has been grown SiC-free, reveals a lower carbon concentration, while the contamination with oxygen is comparable those of sample I or II. Silicon could not be found in such crystals. Detailed information about the impurity concentrations are summarized in Tab. 4.4. Regarding these data, we conclude that n-type conductivity strongly influences the defect related luminescence in the NUV region, while minor variations of the carbon, oxygen or silicon concentrations do not seem to play a crucial role as long as the crystals is insulating.

Sample	Conductivity	$O[10^{19} \text{ cm}^{-3}]$	$C[10^{19} \text{ cm}^{-3}]$	$Si[10^{19} \text{ cm}^{-3}]$
I (Presence of SiC)	insulating	1.1	24	20
II (Presence of SiC)	n-type	2.9	21	33
III (SiC-free)	insulating	0.5	0.2	-

Table 4.4.: SIMS data of the oxygen, carbon and silicon concentrations in insulating and conductive AlN crystal. Sample I and II have been grown in the presence of SiC. Sample III has been grown free of SiC.

N-type and insulating crystals also differ with respect to their absorption characteristics. Figure 4.4 shows normalized transmission spectra of an insulating and an n-type AlN crystal for comparison. Both bulk crystals reveal a pronounced sub bandgap absorption. However, while the insulating sample shows a continuous decrease of the transmittance from 2 eV to 4.5 eV, the n-type crystal exhibits a kink above 3.8 eV. Around 4.5 eV the transmittance drops below the detection limit.



Figure 4.4.: Normalized absorption spectra of an n-type and an insulating AlN crystal.

#### Irradiation damage

We studied the influence irradiation damage on the luminescence properties of AlN. For this purpose, an insulating AlN crystal has been irradiated with 300 keV electrons. Figure 4.5 displays monochromatic CL images of the irradiation damaged region, recorded at 2 eV (a), 2.5 eV (b) and 3.5 eV (c). The irradiated region appears as a bright area with a most adequately pronounced contrast at 3.5 eV. The highlighted border results from the electron beam caustic during the irradiation in the TEM. Complementary, in the VIS region at 2.5 eV or 2 eV the contrast is much weaker.



Figure 4.5.: Monochromatic CL images at 2 eV (a), 2.5 eV (b) and 3.5 eV (c) of the 300 keV electron irradiated area of an insulating AlN bulk crystal.



Figure 4.6.: CL spectra of the electron irradiated and the untreated region of an insulating bulk AlN. The NUV luminescence band has been fitted by two Gauss curves, centered at 3.32 eV (VL<sub>A</sub>) and 3.65 eV (VL<sub>B</sub>). The FWHM of both curves is 560 meV.

The corresponding CL spectra, recorded in the irradiated and untreated region, are displayed in Fig. 4.6 for comparison. In the irradiation damaged region, the NUV luminescence is strongly enhanced and resembles the spectra of n-type AlN crystals.

Electron irradiation experiments have also been carried out on epitaxial AlN<sup>1</sup>. Since these samples exhibit very intense NBE luminescence, the impact of electron irradiation can also be studied in this spectral region. Figure 4.7 shows monochromatic CL images of the irradiation damaged region, recorded at 3.5 eV (a) and 6 eV (b). Similar to the bulk crystals crystals, the irradiated region appears as a bright area, with a most adequately pronounced contrast at 3.5 eV. At 6 eV, the irradiation damaged region appears as a dark spot in the monochromatic image, indicating a decrease of the excitonic related luminescence. The spectra of the irradiation damaged and the untreated region are displayed in Fig. 4.8 for comparison. The increase of the NUV luminescence intensity is accompanied by a small shift of the peak from 3.3 eV to 3.5 eV. The increased luminescence around 2 eV is due to the damage created in the SiC substrate and thus shall be disregarded.



Figure 4.7.: Monochromatic CL at 3.5 eV of epitaxial AlN, irradiated by 300 keV electrons.

<sup>&</sup>lt;sup>1</sup>Sample provided by the group of Amano et al.


Figure 4.8.: CL spectra of the electron irradiated and the untreated region of epitaxial AlN.

#### Single transitions in the NUV region

The position and linewidth of the luminescence in the NUV region varies slightly from sample to sample. Typically, the NUV peak is found between 3.3 eV and 3.6 eV, while the band exhibits a linewidth between 560 meV and more than 700 meV. For exemplification, CL spectra of two different n-type samples, grown under nominally identical conditions, are displayed in Fig. 4.9(a) (sample I) and Fig. 4.9(b) (sample II). The NUV luminescence band of sample I, is centered at 3.32 eV with a FWHM of  $\Gamma = 560$  meV, while in sample II it is centered at 3.5 eV with the FWHM of  $\Gamma = 700$  meV. These spectra indicate, that multiple transitions are overlapping in the NUV region. A linewidth of 560 meV however, was found to be the lower limit of the NUV luminescence band, which suggests, that under these conditions, the NUV luminescence is due to an isolated transition. This particular band shall be denoted as the VL<sub>A</sub> in the following. The second band, which causes the broadening of the VL<sub>A</sub> band to the high energy side, could not be isolated in the spectrum. Its peak position may however be estimated by fitting the NUV luminescence, next to the VL<sub>A</sub> with a second Gauss curve, as it was done in Fig. 4.3, Fig. 4.6 and 4.9(b). For these fits, the FWHM of the both curves were taken to be identical, i.e. ( $\Gamma = 560$  meV). This yields a peak position of the second transition around 3.65 eV, which will be denoted as the  $VL_B$ .



Figure 4.9.: CL spectra of two nominally identical AlN boules.

## 4.4.2. Properties of the VL<sub>A</sub> luminescence

In the following, we will investigate the recombination mechanism of the  $VL_A$  band in greater detail. For this purpose, we carried out excitation density and temperature dependent measurements.

#### Excitation density dependence

Figure 4.10 shows the integrated CL intensity of the VL<sub>A</sub> band with increasing beam current. At beam currents,  $I_{\text{Beam}} < 2.5$  nA, the intensity  $I_{\text{VL}_{\text{A}}}$  exhibits a sublinear dependence in the form of

$$I_{
m VL_A} \propto ({
m I}_{
m Beam})^{0.76}$$

An emerging saturation is observed as the beam current exceeds  $I_{\text{Beam}} > 2.5$  nA.



Figure 4.10.: Integrated intensity of the  $VL_A$  band with excitation density. The slope reveals a sub-linear dependence.

In addition, the excitation density dependence of the VL<sub>A</sub> peak position was investigated at 7 K, 350 K and 450 K. Two selected spectra for each temperature are displayed in Fig. 4.11(a-c), using beam currents of 60 pA and 30 nA. At 7 K, the VL<sub>A</sub> shows a distinct blue shift with increasing excitation density, which impinges on the whole band. The respective peak positions for the full dataset are plotted in Fig. 4.12, revealing a blue shift of 12 meV/decade. At 350 K, the shift is merely caused by a broadening to the high energy side of the VL<sub>A</sub> and at 450 K, the VL<sub>A</sub> is completely insensitive to excitation density.



Figure 4.11.: CL of the VL<sub>A</sub> at for beam currents of  $I_{\text{Beam}} = 30$  nA and  $I_{\text{Beam}} = 60$  pA at (a) 7 K, (b) 350 K and (c) 450 K, respectively.



Figure 4.12.: Position of the  $VL_A$  peak with excitation density at 7 K.

#### **Temperature dependence**

The shift of the VL<sub>A</sub> peak ( $\Delta E_{VL_A}$ ), with respect to its low temperature position, is plotted in Fig. 4.13 (solid line). Starting from 7 K, the position of the VL<sub>A</sub> remains almost constant, followed by a blue shift between 70 K and 200 K. Above 200 K, the VL<sub>A</sub> shows a continuous red shift, which maintains up to 450 K.



Figure 4.13.: Shift of the  $VL_A$  peak position (black solid line). The fit will be discussed in section 4.5

The FWHM of the  $VL_A$  band with temperature is displayed Fig. 4.14. From 7 K to 120 K, the FWHM remains nearly constant while above 120 K, it increases continuously up to 450 K.



Figure 4.14.: Temperature dependence of the VL<sub>A</sub> FWHM.

# 4.5. Discussion

In summary, we found the following experimental results:

- i) Typically, the NUV luminescence is composed of two different transitions. A possible deconvolution yields the  $VL_A$  and the  $VL_B$  band. As the FWHM approaches  $\sim 560$  meV the NUV luminescence band only due to the  $VL_A$ , peaking at 3.3 eV. In summary, the following experimental results have been observed.
- ii) The NUV luminescence ( $VL_A$  and  $VL_B$  band) is strongly enhanced in n-type material, while almost absent in insulating AlN.
- iii) 300 keV electron irradiation damage brings up the NUV luminescence in insulating AlN.
- iv) n-type AlN reveals an additional absorption band between 3.8 eV and 4.5 eV.
- v) The integrated intensity of the  $VL_A$  exhibits a sublinear dependence with increasing excitation density. At high excitation densities, the  $VL_A$  saturates.
- vi) At 7 K, the peak of the  $VL_A$  exhibits a blue shift with increasing excitation density. This shift diminishes at or above 350 K.
- vii) The temperature dependence of the  $VL_A$  peak position shows a blue shift between 100 K and 250 K, followed by a continuous red shift above 250 K.
- viii) The FWHM of the VL<sub>A</sub> is almost constant between 7 K and 200 K. From 200 K to 450 K it increases from 560 meV to 630 meV.

We will start our discussion with the underlying recombination mechanism of the  $VL_A$ . Subsequently, the position of the involved defects within the bandgap will be evaluated, which finally allows us to reflect upon their chemical nature.

#### 4.5.1. Recombination mechanism

At 7 K, the excitation density dependence of the  $VL_A$  shows typical characteristics of a DAP transition, as described in section 1.2.5. Its integrated intensity exhibits a sublinear dependence at low and an emerging saturation at high excitation densities. Sublinear dependencies of DAPs are consistent with other findings (see e.g. Ref. [69,97]). The saturation follows from the fact that the lifetimes and concentrations of the donoracceptor pairs are finite.

In addition, the  $VL_A$  shows the characteristic blue shift of DAP transitions with increasing excitation density, as discussed in section 1.2.5. Potential fluctuations may cause similar blue shifts as e.g. discussed in Ref. [70, 98] but in our case, this effect can be excluded since the blue shift diminishes at and above 350 K. The origin for the diminishing blue shift shall be discussed later on in more detail.

Some DAP transitions can easily be identified due a series of isolated phonon repli-However, in our case, we only observe a broad and unstructured band with a cas. FWHW of  $\Gamma \sim 0.5$  eV. In the following, we will show that this shape is caused by the strong influence of electron-phonon coupling. One way to determine the strength of the electron-phonon coupling, is to fit the temperature dependence of the  $VL_A$  FWHM (see Fig. 4.14), using Eq. (1.20). Least square fitting the data yields a Huang-Rhys factor of S = 8.1 and a phonon energy of  $\hbar \omega = 84$  meV. For polar compounds like AlN or GaN, the electron-phonon coupling typically involves longitudinal optical phonons (LO) phonons. Our phonon energy is considerably below the reported values for LOs in AlN of around 110 meV [95]. However, this is not unexpected and often observed for strongly lattice coupled defects [99]. It might indicate a mixed contribution of local, defect related and lattice phonons. The phonon energy therefore corresponds to an averaged value. Using S = 8.1 and  $\hbar \omega = 84$  meV in Eq. (1.18), we are able to calculate the intensity distribution of the isolated phonon line peaks at low temperatures, as indicated by the triangles in Fig. 4.15. A comparison with a CL spectrum of the  $VL_A$  at 7 K (solid line in Fig. 4.15) shows very good agreement. Noticeably, the fit perfectly resembles the steeper increase on the high energy side, as well as more slowly falling off tail of the VL<sub>A</sub> band. Thus, to some extent the VL<sub>A</sub> band resembles a 'Pekarian' line shape, which is typical for intermediate Huang-Rhys factors. Pure Gaussian line shapes (dashed line), are expected to occur for even larger S values.



Figure 4.15.: Calculated intensity distribution of the isolated phonon replicas for S = 8.1and  $\hbar \omega = 84$  meV (triangles) along with a CL spectrum of the VL<sub>A</sub> (solid line). The Gauss curve (dashed line) illustrates the asymmetric shape of the VL<sub>A</sub>.

Knowing the magnitude of the electron-phonon coupling, we are now able to calculate the threshold and maximum energy for the excitation of the  $VL_A$ , as discussed in section 1.2.3. According to the configuration-coordinate model, the zero-phonon line (ZPL) denotes the threshold energy for the optical excitation of the  $VL_A$ , which occurs at

$$E_{\rm ZPL} = E_{\rm VL_A}(T \to 0 \text{ K}) + (S - \frac{1}{2})\hbar\omega \approx 3.9 \text{ eV}$$

$$(4.3)$$

Hence, photon energies above 3.9 eV are required in order to observe the VL<sub>A</sub> in the emission spectrum. This is in agreement with our photoluminescence measurements, showing that it is not possible to excite the VL<sub>A</sub> using photon energies of 3.8 eV (He-Cd laser). Similar results have also been published by Karel et al. already in 1969, who observed that photoexcitation of a luminescence band around 3.3 eV requires energies above 4 eV [100]. The resonance absorption is expected to occur at

$$E_{\text{Res.}} = E_{\text{VL}_{\text{A}}}(\text{T} \to 0 \text{ K}) + (2S - 1)\hbar\omega \approx 4.6 \text{ eV}$$

$$(4.4)$$

The threshold and resonance energies, i.e.  $E_{\text{ZPL}}$  and  $E_{\text{Res.}}$  are in good agreement with the absorption band in n-type AlN between 3.8 eV and 4.5 eV (see Fig. 4.4). In insulating AlN, this absorption band is absent along with the VL<sub>A</sub>. Considering the emission peak

of the VL<sub>A</sub> around 3.3 eV, this equals a Stokes shift of  $E_S = E_{\text{Res.}} - E_{\text{VL}_A} \approx 1.3 \text{ eV}$ .

We will now turn to the temperature dependence of the  $VL_A$  band, as displayed in Fig. 4.13), which yields some additional information about the underlying recombination mechanism. Starting from low temperatures, the peak of the VL<sub>A</sub> ( $\Delta E_{VL_A}$ ) initially exhibits a blue shift above 100 K, followed by a continues red shift from 250 K to 450 K. In order to identify the influencing factors, which govern this behavior, we will compare the shift of the  $VL_A$  with the narrowing of the AlN bandgap energy. The bandgap narrowing typically equals the shift of the free-A-exciton line ( $\Delta E_{FX_A}$ ), which has been calculated using the parameters from Ref. [27] in the model of Pässler et al. [101] (see dotted line in Fig. 4.14). The bandgap narrowing exhibits a continuous red-shift, which reveals distinct similarities to the  $VL_A$  shift: (i) Up to 100 K, the bandgap energy is almost constant, which is in good coincidence with the position of the  $VL_A$  band. (ii) From 250 K to 450 K, the red shift of  $\Delta E_{VL_A}$  and  $\Delta E_{FX_A}$  are comparable. Noticeably, the bandgap narrowing is larger than the shift of the  $VL_A(\Delta E_{VL_A})$ . This is, however, not unexpected keeping in mind that deep centers are often decoupled from the shift of the bands. Thus, DAP transitions involving such states may show a less pronounced shift than the bandgap.

However, the steep blue shift of the  $VL_A$  above 100 K and the resulting energy gap between  $\Delta E_{FX_A}$  and  $\Delta E_{VL_A}$  of around 60 - 80 meV cannot be explained by the influence bandgap narrowing. Therefore, we relate the blue shift to a conversion of the underlying recombination mechanism. In detail, we propose, that the deviation of  $\Delta E_{FX_A}$  and  $\Delta E_{\rm VL_A}$  above 100 K is caused by a successive conversion of the DAP into a free-to-bound transition. Since the free-to-bound transition occurs at higher photon energies than the DAP, the  $VL_A$  peak shift to higher energies. The constant energetic gap between both curves therefore coarsely corresponds to the thermal activation energy of the thermally activated defect, which is about 60 - 80 meV. Such small values indicate the involvement of a comparatively shallow defect, which reasonably corresponds to the fact that the conversion is already initiated above 100 K. The conversion of the DAP transition also explains, why the characteristic blue shift with increasing excitation density cannot be longer observed around and above 350 K. Noticeably, the electron-phonon coupling of the DAP and the free-to-bound transition are invariant, as the continuously increasing FWHM of the  $VL_A$  above 250 K shows. This implies, that the electron-phonon coupling is entirely related to the deep level, which can not be thermally activated within the considered temperature range.

In order to calculate the position of the deep level within the bandgap, we will assume that the shallow level arises from the donor species, close to the conduction band. Hence, at 450 K, the  $VL_A$  luminescence is due to a free-electron-to-bound-acceptor transition. The position of the acceptor species can then readily be calculated via the relation, given in section 1.2.4.

Using  $E_{\rm g} = 5.9$  eV for the bandgap of AlN at 450 K,  $E_{\rm VL_A} = 3.2$  eV for VL<sub>A</sub> peak position at 450 K and S = p, we obtain  $E_{\rm A} \approx 2$  eV. Thus, the acceptor species, involved in the VL<sub>A</sub> is about 2 eV above the valence band.

### 4.5.2. Chemical nature of the involved defects

In this section, we will discuss the chemical nature of the defects, involved in the NUV luminescence, which encloses the VL<sub>A</sub> and the VL<sub>B</sub>. Our studies revealed, that the underlying defects can be generated in insulating AlN, subsequent to 300 keV electron irradiation, which suggests the involvement of native defects. Relativistic electrons of 300 keV transfer a maximum energy of  $E_T$  to the host atoms, creating knock-on damage in the crystal.  $E_T$  can simply be calculated via the relation

$$E_T = \frac{2(E+2mc^2)E}{Mc^2}.$$
 (4.5)

Hereby, M(m) denotes the mass of the host atom (electron), and E the primary electron energy. According to Eq. (4.5), 300 keV electrons transfer an energy of 31 eV to the Al and 60 eV to the N atom. Unfortunately, reliable data on the displacement energies are not available for AlN. Therefore we have to refer to studies carried out on 4H-SiC. For a rough estimation, this is a useful approach since the host atoms are of comparable mass and the crystalline structure is similar. According to the work of Steeds et al. [102], the displacement energies equal 17 eV for C and 24 eV for Si. Assuming that these values also approximately account for N and Al, respectively, one can expect that both host atoms are displaced. Hence, principally Al-, N vacancies, Al-, N interstitials and different vacancy-complexes have been generated due to the electron irradiation.

The fact that the VL<sub>A</sub> and the VL<sub>B</sub> band emerge in n-type AlN strongly suggests the involvement of n-type compensating centers, which reach low formation energies as the Fermi level approaches the conduction band. This puts some more limitations to the variety of native defect levels discussed above. If we look at the ab-initio calculations [3, 11, 16, 34–38, 103], we can see that isolated Al vacancies (V<sub>Al</sub>) and divacancies (V<sub>Al,N</sub>) [34] attain very low formation energies in n-type AlN. At the same time, we can practically rule out the formation of native interstitial defects in n-type AlN, whose formation energies are considerably higher. According Zhang et al., the position of the triply negatively charged isolated Al vacancy  $V_{Al}^{3-}$  in wurtzite AlN is around 1.8 eV above the VBM [37]. This value is in good agreement with the position of the deep level, involved in the  $VL_A$  transition around 2 eV. Thus, Hence, we propose that isolated Al vacancies is involved in the  $VL_A$  band.

Since the  $VL_B$  luminescence emerges under the same conditions as the  $VL_A$ , this suggests that it might be related to divacancies ( $V_{Al,N}$ ) or other Al-vacancy related complexes, e.g. with oxygen. However, since we were not able to isolate this transition in the spectrum, our results are more speculative. Spatial concentration fluctuations of these acceptor might account for the observed peak shifts of the NUV band.

With regard to the donor species appropriate defects must possess a stable - or at least metastable - shallow level about 60 - 80 meV below the conduction band. Such low thermal activation energies are in good agreement with the underlying donor species, related to the bound exciton NBE<sub>1</sub>. In the following, we will discuss some of the possible defects.

- Nitrogen vacancies in AlN are discussed controversially in literature. According to latest ab initio studies in wurtzite AlN, the shallowest level of the nitrogen vacancy introduces as a negatively charged state, i.e. V<sub>N</sub><sup>3-</sup> about 120 meV below the CB [36]. In contrast, Zhang et al., found that nitrogen vacancies only incorporate as deep donors, more than 1 eV below the CB [37], whereas Stampfl et al., claimed that V<sub>N</sub> is forming a shallow donor in AlN [16]. Experimental evidence for a comparatively shallow nitrogen vacancy comes from the work of Nepal et al. and Zhou et al. [104, 105]. With regard to these inconsistent findings, the discussion whether nitrogen vacancies play a role in the VL<sub>A</sub> transition is inadequate at the moment.
- Oxygen is generally accepted to incorporate as a deep DX, i.e.  $O_N DX^-$  [15, 16, 19, 106–110] center. According to theoretical studies, the thermal activation energy is about 1 eV and therefore much too large [15] to be involved in the VL<sub>A</sub>. However, next to the deep state, the oxygen DX center also possesses a metastable, shallow  $O_N^0$  configuration. McCluskey et al. showed, that the  $O_N^0$  configuration is stable up to about 150 K in Al<sub>x</sub>Ga<sub>x-1</sub>N alloys for x > 0.3 [19], due to the thermal capture barrier. Hence, oxygen in the shallow d<sup>0</sup> configuration could be the underlying donor species in the DAP recombination of the VL<sub>A</sub>.
- Silicon on Aluminum site, i.e. Si<sub>Al</sub> could also account for the shallow donor species in the VL<sub>A</sub>. In the n-type crystals, it is present in concentrations up to 10<sup>20</sup> cm<sup>-3</sup>. The experimental results in Ch. 5 will provide evidence that Si<sub>Al</sub> introduces a shallow state, around 120 meV below the conduction band.

## 4.5.3. Conclusions

In conclusion, we propose that the  $VL_A$  is, at low temperatures, due to a DAP transition, involving an unknown shallow donor, close to the conduction band and isolated Al vacancies. This assignment is in full agreement with the model of Nam et al. and Nepal et al [39,40,111]. At elevated temperatures, the thermal activation of the shallow donor promotes free-electron-to-bound acceptor transitions. The Al vacancy introduces about 2 eV above the valence bandedge.

Hence, the VL<sub>A</sub> luminescence can be used as an indicator for the presence of isolated Al-vacancies in the triply negatively charged state, i.e.  $V_{AI}^{3-}$ , which is particularly interesting for studying n-type compensation mechanisms. However, luminescence in the NUV region cannot be used as an indicator for the oxygen concentration of AlN, as e.g. proposed by Slack et al. [47]. In fact, the NUV luminescence can almost be completely absent although the oxygen never drops below  $10^{19}$ cm<sup>-3</sup> in our bulk crystals. Similar objections came from Strassburg et al. [48]. Concerning the sub-bandgap absorption caused by Al vacancies, we disagree with the conclusions of Lu et al. who neglected their influence for the absorption above 4 eV [112].

The absence of the VL<sub>A</sub> in insulating AlN indicates, that the formation of Al vacancies is inhibited in such crystals due to a low Fermi-level. The shift of the Fermi-level towards the conduction band can be prevented by either growing AlN in a SiC free environment - or by introducing a substantial amount of acceptor, not related to Al vacancies. In this context, carbon on nitrogen site, which forms an acceptor state in AlN [113], could play an important role. In our bulk crystals, its concentration is typically in the order of  $10^{18} - 10^{19}$  cm<sup>-3</sup>, which reasonable high.

# 5. Dopants and traps

In this chapter, we will apply thermoluminescence and admittance spectroscopy for the characterization of traps. Our experimental setup allows the detection of traps with a thermal activation energy up to about 1 eV. Based upon these findings, we will discuss their chemical nature and propose a detailed model for the n-type conductivity in our bulk crystals.

# 5.1. Thermoluminescence

In the following, we will discuss thermoluminescence curves of bulk and epitaxial AlN. For the sake of clarity, these TL curves have coarsely been divided into two temperature regions, i.e. (i) region A from 10 K to 225 K and (ii) region B from 225 K to 450 K. The notation of the defect levels is in ascending order, pursuant to their peak temperature, e.g.  $A_x$  or  $B_x$ .

## 5.1.1. Bulk AIN crystals

Figure 5.1, shows typical TL curves of AlN, grown with and without SiC inside the crucible.



Figure 5.1.: TL curves of AlN bulk crystals grown in the presence (absence) of SiC inside the crucible.

As discussed in section 3.4, AlN grown in the presence of SiC contains, next to a slightly increased C concentration, Si, typically in the order of  $10^{20}$  cm<sup>-3</sup>. Generally, the TL curves from bulk crystals are strongly varying with the probe location, which indicates a spatially inhomogeneous defect distribution. However, we found that substantial TL yield in region A can only be observed from bulk crystals, which have been grown in the presence of SiC.

In Fig. 5.2, we take a closer look at the low temperature region of TL curves from AlN, grown with and without SiC inside the crucible.



Figure 5.2.: Upper curve: TL of a bulk AlN crystal, grown in an SiC-free environment. The TL intensity has been magnified by a factor of 10. Lower curve: TL of an AlN crystal grown in the presence of SiC inside the crucible. The fit (dotted line) was calculated by considering a Gaussian energy distribution of the underlying defect with a concentration maximum at 110 meV and a FWHM of 63 meV.

Both curves have been normalized to their respective maximum, which occurred around  $\sim 350$  K. Due to the low TL yield of the SiC-free grown crystal in this region, the TL curve has additionally been multiplied by a factor of 10. Clearly, the intense low temperature peak A<sub>0</sub>, centered at 55 K, can only be observed in crystals grown in the presence of SiC.<sup>1</sup> Noticeably, A<sub>0</sub> exhibits an anomalously large linewidth and the fit, using

<sup>&</sup>lt;sup>1</sup>The small feature of the SiC-free grown AlN, typically peaking around 65 K - 80 K, has been ob-

the standard analytical expression in section (2.5), does not result in a good agreement with the curve. Comparing TL curves from several, nominally identical crystals reveals, that the peak position and shape of  $A_0$  remains unaffected. We therefore conclude, that the irregular linewidth does not originate from overlapping TL bands but emerges from a quasi-continuous energy distribution of the underlying defect. For the fit, we assume a Gaussian energy distribution with a maximum concentration for thermal activation energy of 110 meV and a full width at half maximum (FWHM) of 63 meV. This increases the linewidth of the fit and a reasonable agreement with the measurement is attained.

Figure 5.3, shows two more TL curves from AlN, grown in the presence/absence of SiC in region A. Due to the low TL yield, the upper TL has been magnified by a factor of 5. Both curves exhibit two additionally TL peaks in temperature region A, which have been denoted as  $A_1$  and  $A_2$ . In contrast to  $A_0$ ,  $A_1$  and  $A_2$  exhibit a regular broadness and the fit reveals thermal activation energies of around 400 meV for  $A_1$  and 500 meV for  $A_2$ .



Figure 5.3.: Upper curve: TL of an AlN crystal (SiC-free). Lower curve: TL of AlN, grown in the presence of SiC. The fit shows the isolated TL peaks (dotted lines) and the composite signal (dashed line).

served irregularly. We relate this TL to minor nonlinearities in the initial heating phase of the TL measurement, which is difficult to control. For this reason, it shall be disregarded.

We will now turn to region B. Substantial TL yield in temperature region B is generally observed from all bulk crystals. Hence, for the following TL curves, we will be no longer distinguish whether the sample has been grown in the presence of SiC or not.

A section of the TL curve in Fig. 5.4 has been fitted by three TL peaks, denoted as  $B_1$ ,  $B_2$  and  $B_4$ . The composite fit is in very good agreement with the TL curve and reveals thermal activation energies of the underlying defects between 625 meV and 840 meV. Noticeably,  $B_4$  is an almost completely isolated TL peak. Between 350 K and 450 K, the TL signal is too unstructured for an accurate deconvolution and will therefore not be evaluated in this curve.



Figure 5.4.: TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks (dotted lines) and the composite curve (dashed line).

The TL curve in Fig. 5.5 has been fitted using four TL peaks, revealing trap levels with thermal activation energies between 635 meV and 1085 meV. Two of the peaks ( $B_2$  and  $B_8$ ) are almost completely isolated, which allows a very reliable fit. The TL curve in Fig. 5.6 has been fitted by two TL peaks, i.e.  $B_7$  and  $B_8$ , revealing defects with thermal activation energies of 905 meV and 1035 meV, respectively.



Figure 5.5.: TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks (dotted lines) and the composite curve (dashed line).



Figure 5.6.: TL curve of bulk AlN (solid line). The fit shows the isolated TL peaks (dotted lines) and the composite curve (dashed line).

The TL curve in Fig. 5.7 has been deconvoluted using three TL peaks, i.e.  $B_1$ ,  $B_2$  and  $B_3$ . The composite fit is in good agreement, revealing defects with thermal activation energies of 625 meV, 665 meV and 710 meV, respectively.



Figure 5.7.: TL curve from insulating AlN (solid line). The fit shows the isolated TL peaks (dotted lines) and the composite curve (dashed line).

## Thermally stimulated conductivity

Thermoluminescence measurements, considered in isolation, are generally only of limited conclusiveness. Thus, in order to corroborate that the observed TL peaks are related to thermal emission of charge carriers from traps into the bands, we additionally carried out TSC measurements.

Thermally stimulated conductivity measurements have only been successful on weakly n-type AlN crystals i.e. AlN grown in the presence of SiC. In contrast to TL, it was found that the TSC curves generally suffer from a very low signal to noise ratio, which makes such curves unsuitable for an accurate determination of defect parameters. Nevertheless, the TSC curves can still be used to validate the emission of charge carriers into the bands.

Figure 5.8 displays a TL and TSC curve in the low temperature region A, which have been recorded simultaneously in the SEM setup. Clearly, all TL peaks in region A coincide with a TSC signals. (In this curve, the TL from  $A_1$  is barely observable due to the strong TL intensity of  $A_0$ ). This clearly validated the the TL peaks in region A are due to thermal emission of charge carriers into the bands.



Figure 5.8.: Simultaneous TL / TSC measurement of a weakly n-type AlN (grown in the presence of SiC).

TSC measurements in the high temperature region B (225 K – 450 K) remained unsuccessful in the SEM setup. Potentially, this is because the electron beam does not provide a sufficiently strong excitation source. For this reason, simultaneous measurements of the TL and the TSC curves could not be carried out. Instead, we performed the TSC measurements in a different setup, using the full spectrum of a XE lamp for excitation. The results are displayed in Fig. 5.9 along with all TL peak positions. A clear correlation is observed for  $B_4$ , while TSC peaks related to B1-B3 are barely observed. Unfortunatley, the detection of TSC peaks above  $B_4$  is prevented due to an increasing dark current.



Figure 5.9.: TSC curve of a weaky n-type AlN (grown in the presence of SiC). This curve was recorded in a different setup using the full spectrum of a XE lamp for excitation.

## 5.1.2. Epitaxial AIN

Thermoluminescence measurements have also been applied for the characterization of traps in epitaxial AlN, which has been provided by different groups. Apparently, the TL curves from epitaxial AlN are almost invariant to the TL probe location, indicating that the defect distribution is spatially very homogeneous.

Figure 5.10(a) shows a TL curve between 10 K and 100 K of AlN <sup>2</sup>, grown by MBE on a SiC substrate. In this region, the TL curve only exhibits a single peak, centered at ~ 62 K. Although the peak temperature is slightly higher as compared to the bulk crystals, we will label this TL peak as  $A_0$ . In contrast the bulk specimen, the peak exhibits a regular broadness and the fit, using the numerical approach (Eq. (2.3)), yields a thermal activation energy of 155 meV.  $A_0$  is the only evaluable TL peak withing the entire temperature range, up to 450 K, as can be seen in the entire TL curve in Fig. 5.10(b). The initial part of a is observed around 450 K.

<sup>&</sup>lt;sup>2</sup>Sample E962 by E. Monroy et al.



Figure 5.10.: (a) Low temperature part of a TL curve from epitaxial AlN, grown by MBE on a SiC substrate.



Figure 5.11.: Lower curve: TL of epitaxial AlN grown by MOCVD on a silicon substrate. Upper curve: TL curve of a bulk AlN crystal (grown in the presence of SiC).

Figure 5.11(lower curve) shows a TL curve from  $AlN^3$  grown on a silicon substrate. The main TL yield is emitted between 200 K to 300 K, exhibiting multiple overlapping peaks. This region has been fitted by three TL peaks, denoted as  $A_2$ ,  $B_1$  and  $B_4$ , revealing thermal activation energies of 515 meV, 590 meV and 860 meV, respectively. Very similar TL curves can be observed from bulk AlN crystals, as the curve in Fig. 5.11 shows. The initial part of the TL signal around 400 K cannot be fully resolved due to the temperature limit of the setup.

Figure 5.12(lower curve) shows a TL curve from another epitaxial sample<sup>4</sup>, grown by MOCVD on a SiC substrate. The curve exhibits a broad band from 200 K to 300 K, which can be fitted by using three TL peaks, denoted as  $A_2$ ,  $B_1$  and  $B_2$ . As for the TL curve in Fig. 5.11, the similarities to the TL from bulk material are very obvious. The thermal activation energies of the underlying defects range from 545 meV ( $A_2$ ) to 640 meV ( $B_2$ ).



Figure 5.12.: TL curve of epitaxial AlN grown by MOCVD on a SiC substrate.

<sup>&</sup>lt;sup>3</sup>Sample 'AZ45' grown by the group of Dadgar et al.

<sup>&</sup>lt;sup>4</sup>Sample grown by the group of Amano et al.

# 5.2. Trap type analysis

Since TL and TSC are principally sensitive to electron and hole traps, the analysis of the trap type requires additional measurements. For this purpose, we carried out electron paramagnetic resonance (EPR), admittance spectroscopy and spectrally resolved TL.

### 5.2.1. Electron paramagnetic resonance

At 7 K, photo-excitation of AlN crystals, grown in the presence of SiC, with light of 500 nm results in an EPR signal, as displayed in Fig. 5.13. After switching off the light source, the signal persists. Heating the sample first causes a narrowing of the EPR signal up to 40 K, followed by a rapid decrease above 60 K, indicating a thermal emission. This EPR signal could also be observed by optical excitation, using wavelengths of  $\lambda > 800$  nm and  $\lambda > 1100$  nm, although in the latter case, the intensity is very low. Similar EPR signals from AlN grown SiC-free could not be observed.



Figure 5.13.: Isotropic EPR signal (g = 1.990) in AlN:Si after prolonged illumination ( $\approx 500 \text{ nm}$ ) at low temperatures. The signal persists up to 60 K.

In Fig. 5.14, the temperature dependent spin density of the EPR signal is displayed along with a TL curve of the same sample. The rapid decrease of the EPR signal coincidences with TL peak  $A_0$ .



Figure 5.14.: Correlation between the decrease of the EPR signal with temperature and the TL peak  $A_0$ .

#### 5.2.2. Electron traps in bulk AIN

While TL and TSC are principally sensitive to both types of traps (electron and hole traps) admittance spectroscopy only reveals majority carrier traps, i.e. electron traps in the n-type crystals. In Fig. 5.15, the frequency and temperature dependence of the conductance G and the capacitance C of an n-type AlN crystal are displayed. An Arrhenius plot of the  $G/\omega$  peaks is shown in Fig. 5.17. The gradient reveals an electron trap with a thermal activation energy of 520 meV and its intersection with the ordinate a frequency of  $\omega_0 \approx 2 \cdot 10^{10} \text{s}^{-1}$ . The fit is in very good agreement with the experimental data over about 3 orders of magnitude. Another admittance measurement of a different n-type bulk crystal is displayed in Fig. 5.16. The  $G/\omega$  plot exhibits two peaks in the curve, indicating the presence of two other electron traps. The analysis of the  $G/\omega$  peaks in an Arrhenius plot, reveals thermal activation energies of 630 meV and 860 meV, as displayed in Fig. 5.18. The intersection points with the reveals  $\omega_0 \approx 5 \cdot 10^{10} \text{ s}^{-1}$  and  $\omega_0 \approx 2 \cdot 10^{12} \text{ s}^{-1}$ , respectively. Both fits show a good linear dependence in the range of 3 orders of magnitude with minor deviations in the high temperature region.



Figure 5.15.: Admittance spectroscopy measurement of an n-type AlN crystals, showing the frequency dependence of the capacitance (C) and the conductance  $(G/\omega)$  with temperature.



Figure 5.16.: Admittance spectroscopy measurement of an n-type AlN crystals, showing the frequency dependence of the capacitance (C) and the conductance  $(G/\omega)$  with temperature.



Figure 5.17.: Arrhenius plot of the  $G/\omega$  peaks from Fig. 5.15.



Figure 5.18.: Arrhenius plot of the  $G/\omega$  peaks from Fig. 5.16.

#### 5.2.3. Spectrally resolved thermoluminescence

In Fig. 5.19, a spectrally resolved TL measurement of an AlN crystal (grown in the presence of SiC) is displayed. Within the entire temperature range i.e. region A and B,

two recombination channels are visible, centered around 650 nm (1.9 eV) and 380 nm (3.3 eV). The latter recombination channel emerges only if the TL intensity becomes very large. These two radiative channels are typically observed defect related luminescence bands in our n-type AlN crystals, as described in chapter 4.



Figure 5.19.: Spectrally resolved TL curve of n-type AlN.

# 5.3. Discussion

# 5.3.1. Summary - trap parameters

Thermoluminescence and admittance spectroscopy investigations revealed numerous defects in bulk and epitaxial AlN with thermal activation energies ranging from 110 meV to about 1 eV.

The trap parameters, determined from TL of bulk AlN are summarized in Tab. 5.1. Generally, these TL curves are strongly varying with the probe location, indicating that the spatial defect distribution is inhomogeneous. Electron traps in bulk AlN have additionally been identified by admittance spectroscopy in weakly n-type crystals. The results are listed in Tab. 5.2.

The defect parameter, determined from TL curves of epitaxial AlN are listed given in Tab.

TL peak	E [meV]	s $[10^{10} \text{ s}^{-1}]$	Peak [K]	TSC	Remarks
A <sub>0</sub>	110	1	55	$\checkmark$	Only in n-type AlN
$A_1$	393	1	171	$\checkmark$	Incr. in n-type AlN
$A_2$	505	2	210	$\checkmark$	Incr. in n-type AlN
$B_1$	625-635	10	245	-	
$B_2$	665-680	10	266	?	
$B_3$	710	10	277	-	
$B_4$	840-860	200	300	$\checkmark$	
$B_7$	905	1	375	-	
$B_8$	1035-1085	5	420	-	

5.3. In contrast to the bulk material, the TL from such specimen is almost insensitive to the probe volume, indicating a much more homogeneous spatial defect distribution.

Table 5.1.: Defects determined by TL in bulk AlN.

Associated TL peak	E [meV]	$\omega_0 \ [10^{10} \ {\rm s}^{-1}]$
$A_2$	520	3
$B_1$	625	5
$B_4$	860	200

Table 5.2.: Electron traps determined by admittance spectroscopy in n-type AlN.

TL peak	E [meV]	s $[10^{10} \text{ s}^{-1}]$	Peak [K]	Remarks
A <sub>0</sub>	155	100	62	
$A_2$	515 - 545	3-20	210	
$B_1$	590 - 595	5-20	240	Low accuracy.
$B_2$	640	10	260	Low accuracy.
$B_4$	860	200	300	Low accuracy.

Table 5.3.: Defect parameters determined by TL in epitaxial AlN crystals.

#### Thermoluminescence peak A<sub>0</sub>

The shallowest defect, which has been identified in bulk and epitaxial AlN, is related to the TL peak  $A_0$ . We attribute this TL peak to a silicon, incorporating on aluminum site (Si<sub>Al</sub>). Our assignment is based on the following observations: First,  $A_0$  is exclusively observed in TL curves from AlN, which have been grown in the presence of SiC and thus contain a substantial amount of Si (see section 3.4 for details). Second, AlN crystals containing Si exhibit an EPR signal, which is identical to the one described in the work of Zeisel et al. [13]. In agreement with their attribution, we relate this EPR signal to Si on Al site, forming an impurity band. The decrease of the EPR signal around 60 K indicates a thermal activation process, which is coincident with the emerging TL peak  $A_0$ . Thus, the TL peak  $A_0$  is due to thermal emission of electrons from the silicon impurity band into the conduction band, which also causes the TSC signal.

Characteristic properties of an impurity band have been observed in the EPR measurements of bulk AlN, showing a the narrowing of the EPR signal from 10 K to 30 K. This effect is related motional narrowing, which causes a decrease of the exchange interaction between the electrons, as described in Ref. [114]. The thermal emission of electron from an energetically distributed impurity band reasonably explains the anomalous linewidth of  $A_0$  in the TL curves from bulk crystals. Moreover, the silicon concentration, which is, according to our SIMS measurements typically the order of  $10^{20}$  cm<sup>-3</sup>, is reasonably high for an impurity band formation.

A similar low temperature TL peak at 62 K has been found in MBE grown AlN. Although experimentally less validated, it is likely that this peak is also related to  $Si_{Al}$ . Although the growth temperatures are considerably lower, the silicon dopant might have been provided by the SiC substrate during the growth, similar to the bulk crystals. Noticeably, in the epitaxial sample,  $A_0$  is slightly shifted to higher temperatures and the peak reveals a regular broadness. This suggests that the silicon concentration is too low for an impurity band formation and therefore, the TL peak refers to the isolated point defect. This also explains, why the determined thermal activation energy is slightly higher.

Comparing the thermal activation energies, for  $Si_{Al}$  of 110 meV in the bulk (impurity band) and 155 meV (point defect) in epitaxial AlN, with results in literature reveals only partial agreement. In fact, the determined thermal activation energies for AlN:Si are widely scattered valued in literature, ranging from 86 meV [20], 180 meV [18] up to 282 meV [21]. We will come back later to this point, in conjunction with our n-type conductivity model.

#### Thermoluminescence peaks $A_2$ , $B_1$ and $B_4$

Admittance measurements revealed deep electron traps, 520 meV, 625 meV and 860 meV below the conduction band. The shallowest level is in good agreement with the  $A_2$ trap, determined from TL analysis, indicating that they refer to the same trap. The frequency factor s and  $\omega_0$  are also in the same order of magnitude, which corroborates our assignment. Also,  $A_2$  is accompanied by a TSC signal, which verifies the emission of charge carriers into the bands. Hence, we assign the TL peak  $A_2$ , to an electron trap around 520 meV below the conduction band. Although the TL yield of  $A_2$  is increased in AlN, grown in the presence of SiC, it can also also be found in AlN grown SiC-free. Therefore, it is not conclusive, whether this indicates an altered concentration of the underlying trap. Alternatively, an increased TL yield might, for example, also result from the different initial trap occupation. Keeping in mind that doping AlN with silicon severely affects the position of the Fermi level, this matter might have a substantial influence on trap occupation ratio - and thus the TL yield.

Analogous to our discussion concerning  $A_2$ , we can associate the two other electron traps 625 meV and 860 meV below the conduction band. with the TL peaks  $B_1$  and  $B_4$ . While  $B_4$  is clearly accompanied by a TSC signal, the results concerning  $B_1$  are less conclusive. Thus, at least for  $B_4$ , we can unequivocally confirm the thermal emission of charge carriers into the bands. However, the fits of  $B_1$  and  $B_4$  yield thermal activation energies of 625 - 635 meV and 840 - 860 meV, respectively, which is in good agreement with our admittance spectroscopy results. The same accounts for the frequency factors 's', which are comparable with the  $\omega_0$  values. Noteworthy in this context is the higher frequency factor s (or  $\omega_0$ ) of  $B_4$ , which is the order of  $10^{12}$  s<sup>-1</sup>.

The peaks  $A_2$ ,  $B_1$  and  $B_4$  also appear in TL curves from epitaxial AlN, which suggests the presence of identical electron traps. This is quite surprising, since the growth conditions, particularly the temperature regimes, are entirely different. In TL curves from MBE grown AlN however, none of these peaks can be found, indicating the absence of such traps.

#### Thermoluminescence peaks $A_1$ , $B_2$ , $B_3$ , $B_7$ and $B_8$

The majority of the observed TL peaks cannot be clearly attributed to a specific trap type due to the lack of data from e.g. EPR or admittance spectroscopy measurements. However, our spectrally resolved TL analysis gives some evidence, that the TL peaks  $A_1$ ,  $B_2$ ,  $B_3$ ,  $B_7$  and  $B_8$  also refer to electron traps in the upper half of the bandgap. As can be seen in Fig. 5.19, the whole TL between 10 K and 450 K is emitted in identical recombination channels, i.e. the VIS band and the VL<sub>A</sub>. This suggests, that the underlying traps refer to the same kind, i.e. electron traps, as described in section 2.1.5. Noticeably, the emerging VL<sub>A</sub> band in the TL around 350 K, which is at these temperatures due to a free-electron-to-bound-acceptor recombination (see Ch. 4), perfectly conforms the underlying simple model of thermoluminescence. If all these defects refer to electron traps, they should principally also be detectable by admittance spectroscopy (except  $A_1$ which is above the Fermi-level). Obviously, this is not the case. We relate this fact to a generally low concentration of these traps. This interpretation is partly supported by the fact that the TSC signals of  $B_2$  and  $B_3$  are barely observed. With regard to  $B_7$  and  $B_8$ , however, our results are not conclusive since their TSC signal is prevented from detection due to the increasing dark current.

None of these defects, except potentially  $B_2$ , can be observed in TL curves from epitaxial AlN samples. This seems to indicate the absence of the underlying traps. <sup>5</sup>

#### Oxygen related thermoluminescence

In literature, the TL related around 350 K  $(B_7)$ , is often discussed in conjunction with oxygen impurities [30, 31, 115, 116]. Rosa and Tale conducted the most comprehensive studies in this context. They attributed the TL around 350 K to oxygen, incorporating on nitrogen site, i.e. O<sub>N</sub> and determined a thermal activation energy of around 600 meV, using the very sophisticated fractional glow technique [32]. Although our result indicate the involvement of electron traps in this region of the TL curve, we have objections against the attribution to oxygen impurities. First, the TL curves of Rosa and Tale exhibited broad and unstructured TL bands around 350 K, suggesting a large amount of overlapping peaks. This makes a distinctive attribution to one particular defect extremely difficult, especially if this assignment is only based on TL measurements. Moreover, they determined an apparently low frequency factor for  $O_N$  in the order of  $10^8 \text{ s}^{-1}$ , which lacks a reasonable explanation. Second, oxygen-related TL around 350 K is completely absent in epitaxial AlN, although impurity concentrations in such samples are typically in the order of  $\sim 10^{17}$  cm<sup>-3</sup>. Third, our analysis of the TL around 350 K indicates the involvement of electron traps with much larger thermal activation energies than 600 meV, using reasonable frequency factors in the order of  $10^{10}$  s<sup>-1</sup>.

Instead, we propose that oxygen related TL should emerge at much higher temperatures, which is supported by findings in literature. According to Lee et al., the critical Al content in  $Al_xGa_{x-1}N$  alloys for the stable  $O_N$  donor is around x = 0.4 [117]. Above, this value, it relaxes into the deep DX configuration. Deep centers are (in good approximation) decoupled from the shift of the respective bandedge, which implies in our case, that the thermal activation energy of the  $O_N DX^-$  level approximately scales with the shift of the conduction band up to x = 1. According to Nepal et al., the  $Al_xGa_{x-1}N$  bandgap is given by [39].

$$E_g(\operatorname{Al}_x\operatorname{Ga}_{1-x}\operatorname{N}) = (1-x)E_g(\operatorname{Ga}\operatorname{N}) + xE_g(\operatorname{Al}\operatorname{N}) - bx(1-x)$$
(5.1)

with the bowing parameter b = 1 eV,  $E_g(AlN) = 6.1$  eV and  $E_g(GaN) = 3.5$  eV for the bandgap of AlN and GaN, respectively. The conduction/valence band offset is taken to be 70/30 [118]. As can be seen in Fig. 5.20, this would imply thermal activation energies

<sup>&</sup>lt;sup>5</sup>Since the epitaxial samples reveal TL peak above 400 K, we can exclude that the traps, deeper than  $B_4$ , are prevented from detection due to the attainment of the thermal equilibrium.

around 1.2 eV for  $O_N DX^-$ , which is twice as large as the value determined by Rosa and Tale. Larger activation energies around 1 eV for the  $O_N DX^{(-)}$  have also been suggested by ab-initio calculations [15].



Figure 5.20.: Estimation of the O<sub>N</sub> DX<sup>-</sup> level throughout the entire Al<sub>x</sub>Ga<sub>x-1</sub>N alloy. The decoupling from the CB occurs at x = 0.4

A TL peak, corresponding to a defect with a thermal activation energy of 1.2 eV (assuming reasonable frequency factors of  $10^{10} \text{ s}^{-1}$ ), is expected to occur around 500 K, as the fit in Fig. 5.21 shows, which exceeds the temperature limit of our experimental setup.



Figure 5.21.: Expected position of the TL peak, related to  $O_N$  in its deep  $DX^{(-)}$  configuration.

In summary, the TL peaks  $A_2$ ,  $B_1$  and  $B_4$  are related to electron traps. All other TL peaks also refer to electron traps which are however too low in concentration. Furthermore, it is unlikely that the TL around 350 K ( $B_7$ ) is related to  $O_N$ . Thus, a clear identification of an oxygen related TL peak remains open.

# 5.4. Metastable properties of traps

In this section, we will try to find evidence, whether some of the defects, discussed above, show metastable characteristics. In this context, their effect on the electrical and optical properties will be discussed. Of particular interest is whether we find evidence for a Si  $(A_0)$  related DX transition.

#### 5.4.1. Persistent photoconductivity

All n-type bulk crystals reveal persistent photoconductivity subsequent to illumination at temperatures below 180 K. In Fig. 5.22, the temperature dependent conductivity of a cooling and a heating cycle between 15 K and RT is displayed.



Figure 5.22.: Temperature dependence of the conductance before and after illumination with light of 514 nm and  $\sim 800$  nm

While cooling the sample down in the dark to 15 K with an applied bias voltage of 15 V, the conductivity decreases until, at  $\sim 60$  K, it drops below the detection limit of the electrometer. After reaching the low temperature limit of 15 K, the sample has been illuminated with monochromatic light of 514 nm (800 nm). This results in an increased conductivity of several orders of magnitude, which persists after the light source is switched off. After a relaxation step at 15 K for about 10 minutes, the sample is heated linearly, while the conductance is recorded. For both excitation wavelengths, principally identical results can be observed: Up to 60 K, the conductivity slightly increases, followed

by a small decrease of about one order of magnitude. Above 120 K, the conductivity increases again and the heating cycle intersects the cooling curve at  $\approx 170$  K.

### 5.4.2. Temperature dependent TL yield

The following TL curves have been recorded after sample excitation at different temperatures i.e. 7 K, 100 K, 120 K and 140 K, as displayed in Fig. 5.23. Although the electron beam settings and the excitation times of 30 s are identical for all measurements, the TL yield of the  $A_2$  increases as the excitation temperature approaches 140 K. In addition, the TL peak  $A_2$  slightly shifts towards lower temperatures. All other TL peaks in the curve remain almost unaffected.



Figure 5.23.: Various TL curves recorded after sample excitation at different temperatures. The isolated TL peaks (dotted lines) were calculated by varying the parameters pursuant to Tab. 5.4.

Excitation Temp [K]	E [meV]	$s [s^{-1}]$	$c_n^{\rm T} [{\rm cm}^3 {\rm s}^{-1}]$	$c_n^{\rm R} [\ {\rm cm}^3 {\rm s}^{-1}]$	Trap filling
7	545	$3x10^{11}$	$4x10^{-10}$	$1 x 10^{-9}$	100~%
100	545	$3x10^{11}$	$4x10^{-10}$	$1 x 10^{-9}$	56~%
120	545	$3x10^{11}$	$4x10^{-10}$	$1 x 10^{-9}$	31~%
140	545	$3x10^{11}$	$4x10^{-10}$	$1 x 10^{-9}$	8 %

Table 5.4.: TL fit parameters.

The TL curves in the figure have been fitted by the numerical approach using the parameters given in Tab. 5.4. For these fits, all defect parameters, except the initial trap occupation ratio, remained constant. Setting the trap occupation ratio for sample excitation at 140 K to 100 %, requires a reduction to 8 % to fit the TL peak for the 7 K measurement. All fits exhibit very good agreement with all the curves, including the small shift towards higher temperatures as the intenstity decreases. This is a well known effect in TL spectroscopy, which is related to an enhanced re-trapping due to the larger amount of unoccupied states. The determined thermal activation energy for A<sub>2</sub> is 545 meV, using a frequency factor of  $s = 3 \cdot 10^{11} \text{ s}^{-1}$ .

#### 5.4.3. Competitive non-radiative recombination

Figure 5.24(a) shows a CL spectrum of a bulk crystal exhibiting the VL<sub>A</sub>, as well as luminescence in the VIS region. The temperature dependence of their integrated intensities, displayed in Fig. 5.24(b), have been determined by Gauss fits, as indicated in the figure. The integrated intensities of the VL<sub>A</sub> and the VIS luminescence exhibit a uniform behavior with temperature between 7 K and 450 K. We repeated the temperature dependent measurement of the VIS band with an appropriate edge filter to exclude the influence of the 2nd order VL<sub>A</sub> band, showing no differences. Also, the measuring cycle i.e. starting at low temperature and subsequent heating or starting at high temperatures and subsequent cooling has no influence on these results.



Figure 5.24.: (a) CL spectrum showing the  $VL_A$  and a VIS luminescence band. Both bands have been fitted by one Gauss curve, respectively. (b) Temperature dependence of the integrated  $VL_A$  and VIS intensities.

The application of a simple thermal formula reveals an 'activation energy' of 67 meV for

the initial decrease of the  $VL_A$  between 100 K and 200 K.



Figure 5.25.: Temperature dependence of the integrated  $VL_A$  luminescence intensity. The application of the simple thermal quenching formula in Eq. (1.23) reveals an 'activation energy' of 67 meV.

The temperature dependence of the VIS band was recorded for varying beam currents. Since the luminescence yield becomes very small for low beam currents, a broadband photomultiplier with a bandpass filter, centered around 1.8 eV (bandwidth 0.25 eV) was used for detection. Furthermore, in order to exclude a possible contribution by thermo-luminescence, the measuring cycle was reversed, i.e. starting at high temperatures and measuring while cooling down. As can be seen in Fig. 5.26(a), increasing the excitation density causes (i) a shift of the relative intensity minimum to higher temperatures, (ii) a more pronounced decrease of the luminescence intensity between 100 K and 200 K and (iii) a flattening of the increasing intensity above 350 K. Figure 5.25 shows the temperature dependent intensity of the VL<sub>A</sub>luminescence band.


Figure 5.26.: (a) Temperature dependence of the integrated VIS luminescence intensity using different excitation densities, recorded with a bandpass filter centered at 1.8 eV. (b) Calculated temperature dependence of the radiative recombination channel 'R' as drafted in Fig. 5.28 by solving Eq. 5.3.

## 5.5. Discussion

In summary, we observe (i) persistent photo-conductivity (PPC), (ii) a TL yield of  $A_2$ , which strongly depends on the sample temperature for excitation and (iii) a uniform temperature dependence of the luminescence intensity. We relate all these phenomena to the presence of a trap with a thermal capture barrier, such as a DX center.

While the PPC effect is a typical characteristic of such a defect, the two latter observations require further explanations.

### Temperature dependent TL yield of A<sub>2</sub>

The temperature dependent TL yield of  $A_2$  results from a varying occupation ratio of the DX-like electron trap. As we have discussed in chapter 1, the introduction of a DX center into a semiconductor results in shallow d<sup>+</sup>, d<sup>0</sup> states and a negatively charged ground state DX<sup>-</sup>. For exemplification, we take (i) the d<sup>+</sup> state as to be in resonance with the conduction band and (ii) the DX<sup>-</sup> level, as to be unoccupied by electrons (steady-state conditions). This situation is depicted Fig. 5.27(a), which we consider as the initial situation after cooling down the sample in the dark<sup>6</sup>.



Figure 5.27.: Illustration for the increased TL yield of  $A_2$ , at elevated sample excitation temperatures.

Excitation of the sample at low temperatures, i.e.  $\approx 7$  K, creates free electron-hole pairs in the bands. This causes a conversion of d<sup>+</sup> states into their neutral charge state d<sup>0</sup>, which we also consider as to be in resonance with the conduction band (see Fig. 5.27(b)). However, due to the thermal capture barrier for electrons, the transformation into the DX<sup>-</sup> configuration is prevented. Hence, for sample excitation at low temperatures the population of the DX<sup>-</sup> ground state is very inefficient and thus the TL yield of A<sub>2</sub> is small <sup>7</sup>.

In contrast, for sample excitation at elevated temperatures, i.e.  $T \approx 140$  K, the electrons can easily overcome the thermal capture barrier and the d<sup>0</sup> level relaxes into the DX<sup>-</sup> ground state. This enables an efficient population of the DX ground state during the excitation process. Thus, the occupation ratio and correspondingly, the TL yield of A<sub>2</sub>, increases.

<sup>&</sup>lt;sup>6</sup>In our n-type crystals, this is not the case since the Fermi-level is pinned at the DX<sup>-</sup> state. However, due to strong compensation by deep acceptors in the lower half of the bandgap, the DX<sup>-</sup> steady-state occupation is only partial and thus, the considerations are essentially identical. Details will be given in section 5.6

<sup>&</sup>lt;sup>7</sup>Minor contributions to the occupation of the DX-like ground state may though be attained during the heating step, i.e. the actual TL measurement. However, competitive radiative and non-radiative processes also have to be considered in this context, which impede the efficiency of this 'indirect' occupation process.

Hence, an electron trap, about 520 meV below the conduction band, shows DX-like characteristics. A thermal electron capture barrier prevents its occupation at low temperatures.

### Temperature dependence of luminescence

The presence of a DX-like electron trap also affects the temperature dependent luminescence yield of the bulk crystals. As can be seen in Fig. 5.24, the intensities of the  $VL_A$  and the VIS band show a uniform temperature dependence. Keeping the numerous bands in mind, which are involved in the defect related luminescence of AlN, it is implausible that such a behavior results from thermal quenching effects. For example, Mason et al. identified 7 different transitions in the VIS region [119]. Therefore, a much more plausible explanation for this effect is, that their luminescence yield is mainly governed by the free electron-hole concentration in the bands.

Deep traps in semiconductors are known to reduce lifetimes of electrons and holes due to the fact that they may function as non-radiative pathways. In our case however, the temperature dependence of the defect related luminescence cannot be explained by the presence of a simple, deep trap level, since in this case it is impossible to understand the decrease of the luminescence intensity with increasing temperature. Instead, this requires a trap with a strongly temperature dependent capture cross-section, such as DX-like centers. Evidence for the presence of such a defect in AlN come from the temperature dependent TL measurements, as discussed above.

Qualitatively, the presence of a DX-like center results in the following effects: For above bandgap excitation at low temperatures, i.e. (T ~ 10 K, the electron capture rate of the deep,  $DX^-$  level, is almost negligible due to a thermal capture barrier. Therefore, the e-h concentration in the bands is not affected by its presence. However, as the temperature is increased, the electrons can overcome the thermal capture barrier, which opens an effective, non-radiative channel (assuming a non-negligible hole capture rate). As a consequence, the electron-hole density in the bands and concurrently all luminescence bands decrease in the same manner. The initial decrease of the luminescence efficiency with increasing temperature (see 5.25) therefore reflects the overcome of the thermal capture barrier, which is at least 60 meV <sup>8</sup>. As the temperature is further increased, the thermal emission of electron emission from the DX<sup>-</sup> center becomes crucial, which causes the free e-h density in the bands to increase again. Correspondingly, at elevated temperatures, the defect related luminescence also increases as it can be observed in in Fig. 5.24 above ~ 220 K.

<sup>&</sup>lt;sup>8</sup>This value can only account as a crude approximation since the temperature dependence of the capture coefficient does not at all have a simple exponential form.

In order to get a more quantitative insight into our quenching model, the we will now calculate the temperature dependent luminescence intensity. For this purpose, we assume a luminescence quenching model, as displayed in Fig. 5.28, which considers only two defect states, i.e. a recombination center 'R', and a (DX-like) trap with a thermal capture barrier 'T'.



Figure 5.28.: Simplified luminescence quenching model used for the calculation.

The interactions of 'R' are restricted to electron (hole) capture from the conduction band (valence band) with the capture coefficient  $c_n^R$  ( $c_p^R$ ). Hereby, we consider that electron capture into 'R' represents the integrated luminescence of AlN. Thermal emission of electrons or holes from 'R' is excluded, which makes the luminescence intensity exclusively depend on the the free e-h concentration in the bands. The interactions of 'T' are limited to electron (hole) capture from the conduction band (valence band)  $c_n^T$  ( $c_p^T$ ). The electron capture coefficient is assumed to have a temperature dependence in the form of

$$c_n^{\mathrm{T}}(T) = c_n^{\mathrm{T}}(T = \inf) \cdot \exp(-\frac{\mathbf{E}_{\mathrm{b}}^{\mathrm{T}}}{\mathbf{k}T}).$$
(5.2)

with  $E_b^T$  as the thermal capture barrier and  $c_n^T(T = \inf)$  as the maximum capture coefficient. In addition, we will allow thermal emission of electrons from the trap into the conduction band at an emission rate of  $e_n^T$ .

The calculation was carried out by solving the set of rate equations in Eq. 5.3. All parameter are given in Tab. 5.5. Hereby, typical capture coefficients have been assumed for 'R' in the order of  $1 \cdot 10^{-12}$  cm<sup>3</sup>s<sup>-1</sup>. For the DX-like trap 'T', we use a thermal activation energy of  $E^T = 545$  meV, as determined by TL analysis and a thermal capture barrier of  $E_b^T = 67$  meV, as deduced by the temperature dependent luminescence yield. The electron capture coefficient for  $T \to \infty$  is taken to be at  $4 \cdot 10^{-10}$  cm<sup>3</sup>s<sup>-1</sup>, from the

TL analysis in Fig. 5.23, while the hole capture coefficient is only  $1 \cdot 10^{-14} \text{ cm}^3 \text{s}^{-1}$ .

Electrons at 'T'  

$$\underbrace{\frac{dn^{\mathrm{T}}}{dt}}_{\text{Free electrons}} = N^{\mathrm{T}} \left[ c_n^{\mathrm{T}} n(1 - f^{\mathrm{T}}) - c_p^{\mathrm{T}} p f^{\mathrm{T}} - e_n^{\mathrm{T}} f^{\mathrm{T}} \right]$$
(5.3a)

$$\frac{dn}{dt} = g - N^{\mathrm{T}} \left[ c_n^{\mathrm{T}} n(1 - f^{\mathrm{T}}) - e_n^{\mathrm{T}} f^{\mathrm{T}} \right] - N^{\mathrm{R}} c_n^{\mathrm{R}} n(1 - f^{\mathrm{R}})$$
(5.3b)  
Electrons at 'R'

$$\frac{dn^{\mathrm{R}}}{dt}_{\mathrm{Free \ holes}} = N^{\mathrm{R}} \left[ -c_{p}^{\mathrm{R}} p f^{\mathrm{R}} + c_{n}^{\mathrm{R}} n (1 - f^{\mathrm{R}}) \right]$$
(5.3c)

$$\widehat{\frac{dp}{dt}} = g - N^{\mathrm{R}} c_p^{\mathrm{R}} p f^{\mathrm{R}} - N^{\mathrm{T}} c_p^{\mathrm{T}} p f^{\mathrm{T}}$$
(5.3d)

Parameter	Value	Description
$N^{\mathrm{T}}$	$1 \cdot 10^{19} \text{ cm}^{-3}$	Concentration 'T'
$E^{\mathrm{T}}$	545  meV	Thermal activation energy 'T'
$E_{\rm b}^{\rm T}$	67  meV	Electron capture barrier 'T'
S	$3 \cdot 10^{11} \mathrm{\ s}^{-1}$	Frequency factor 'T'
$c_n^{\mathrm{T}}(T=\infty)$	$4 \cdot 10^{-10} \mathrm{~cm^{3}s^{-1}}$	Capture coefficient electrons 'T'
$c_p^{\mathrm{T}}$	$1 \cdot 10^{-14} \mathrm{~cm^{3}s^{-1}}$	Capture coefficient holes 'T'
$N^{\mathrm{R}}$	$1 \cdot 10^{19} \ {\rm cm}^{-3}$	Concentration recombination center 'R'
$E^{\mathbf{R}}$	$\infty$	Thermal activation energy 'R'
$c_n^{\mathrm{R}}$	$1 \cdot 10^{-11} \mathrm{~cm^{3}s^{-1}}$	Capture coefficient electrons 'R'
$c_p^{ m R}$	$1\cdot 10^{-11}~{\rm cm^3 s^{-1}}$	Capture coefficient holes 'R'

Table 5.5.: Parameters used for the calculation of the luminescence quenching.

The temperature dependent luminescence intensity  $I(T) \propto n^{\mathbb{R}} \cdot p \cdot c_p^{\mathbb{R}}$ , is displayed in Fig. 5.26(b) for 3 different effective generation rates, i.e.  $g = 1 \cdot 10^{10} \text{ s}^{-1}$ ,  $g = 1 \cdot 10^{13} \text{ s}^{-1}$  and  $g = 1 \cdot 10^{16} \text{ s}^{-1}$ . All curves have been normalized to their respective maximum. Clearly, the simulation, based on the model sketched in Fig. 5.28, resembles all major trends of the defect related temperature dependence: (i) The luminescence intensity decreases above 100 K and subsequently increases again around 200 K due to thermal emission of electrons from the non-radiative recombination center 'T'. (ii) The relative minimum of the luminescence intensity is shifted to higher temperatures as the excitation density

is increased. (iii) The initial decrease of the luminescence intensity is getting more pronounced as the excitation density is increased.

In conclusion, we relate the temperature dependent intensity of the defect related luminescence to the presence of a metastable DX-like electron trap, around 500 meV below the conduction band. Due to a thermal capture barrier for electrons, which is about 60 meV, this trap causes a decrease of the luminescence efficiency with increasing temperature. This mechanism might explain the generally low thermal activation energies (60 - 120 meV), determined by luminescence quenching experiments in AlN, e.g. Refs. [120, 121].

### 5.6. n-type conductivity and compensation mechanisms

Based upon our findings in this and chapter 4, will now develop a comprehensive model for the n-type conductivity in our bulk crystals.

The net donor concentration in our bulk crystals can be determined by capacitancevoltage (C-V) measurements. Figure 5.29(a) and 5.29(b) show C-V measurements of two n-type AlN crystals, grown in different runs. By checking the polarity of the Schottky diode, n-type conductivity can be deduced. The capacitance of the Schottky diode was found to be very low at RT, which implies rather large thermal activation energies of the underlying defects. Therefore, the CV measurements have been carried out at 500 K, when the capacitance showed saturation at a sweep frequency of 100 Hz. The net donor concentration can be calculated from the fit of the  $C^{-2} - V$  dependence. Both samples exhibit similar values in the mid of the  $10^{17}$  cm<sup>-3</sup>. While approaching forward-bias, the minor deviations indicate a decrease of the net donor concentration near the surface of the specimen.



Figure 5.29.: CV measurements of two different, weakly n-type bulk crystals, grown in different runs.

Thus, the fluctuations of the net-donor<sup>9</sup> concentrations are very small from sample to sample, while the Fermi levels varies between 500 meV ( $A_2$ ) and 650 meV.

### 5.6.1. Discussion

#### n-type conductivity model

We will now discuss the origin for the n-type conductivity in our bulk crystals, as well as the most important compensation centers. We relate the n-type conductivity to the incorporation of silicon on aluminum site, i.e. Si<sub>Al</sub>, forming a impurity band about 110 meV below the conduction band. This is simply justified by the fact that n-type conductivity can only be observed in crystals, which contain a considerable amount of Si. However, our samples are highly compensated. Typically, the Si concentration is the order of  $10^{20}$  cm<sup>-3</sup>, which is about three orders of magnitude above the actually measured net donor concentration. Thus, we additionally take acceptors into account, incorporating in the lower half of the bandgap  $(A^{-})$ . Evidence for their presence in our n-type crystals has been discussed in Ch. 4 in conjunction with Al vacancies. Since the Fermi level is about 500 - 650 meV below the conduction band, which is considerably below the Si impurity band, we also have to take traps in the upper half of the bandgap into account. In our model, we we will consider both, acceptor-like  $(T^{-})$  and donor-like  $(T^+)$  traps. Evidence for the presence of such states have been identified in this chapter. For the moment, we will disregard the metastable character of the  $A_2$  trap but we will come back later to this point.

A sketch of our n-type conductivity model is displayed in Fig. 5.30. With regard to the concentrations  $Si_{Al}$ ,  $A^-$ ,  $T^-$  and  $T^+$ , principally two configuration are possible, with the Fermi-level in the upper half of the bandgap.

<sup>&</sup>lt;sup>9</sup>Due to the presence of acceptor like traps in the upper half of the bandgap, it is not fully correct to talk about a 'net-donor' concentration. However, for convenience we will stick to this terminus.



Figure 5.30.: Proposed model for the weak n-type conductivity in AlN bulk crystals.

- **Configuration I** The electrons, provided by the silicon impurity band, are almost entirely compensated by deep acceptors (A<sup>-</sup>) in the lower half of the bandgap. Hence, the concentration of (A<sup>-</sup>) is in the order of ~  $10^{20}$  cm<sup>-3</sup>. Due to the fact that the Fermi is below the Si<sub>Al</sub> impurity band, all uncompensated electrons must be trapped at at acceptor-like traps (T<sup>-</sup>) between 520 meV and 860 meV below the conduction band. This determines their minimum concentration to ~  $10^{17}$  cm<sup>-3</sup> in sum. From the fact that the net donor concentration has been observed regularly, one can infer that donor-like traps (T<sup>+</sup>), do not substantially contribute to the n-type conductivity i.e. T<sup>+</sup>  $\ll 10^{17}$  cm<sup>-3</sup>, since otherwise the net-donor concentration would be more instable.
- **Configuration II** In this model, the electrons from the silicon impurity band are fully compensated by deep acceptors (A<sup>-</sup>) in the lower half of the bandgap. Thus, the concentration of (A<sup>-</sup>) must be at least in the order of  $\sim 10^{20}$  cm<sup>-3</sup>. Therefore, the n-type conductivity is caused due to the presence of deep, donor-like traps (T<sup>+</sup>) in the upper half of the bandgap. Hereby, the concentrations of T<sup>+</sup> must precisely balance the compensation of silicon by the deep acceptors to a net donor concentration of  $\sim 10^{17}$  cm<sup>-3</sup>.

We consider configuration I to be much more convincing, compared to configuration II.

In the latter scenario, the net donor concentration is determined by the concentration of  $Si^+$ ,  $A^-$  and  $T^+$ , which is a highly fragile balance and therefore in sharp contrast with a stable net donor concentration, as observed regularly.

In contrast, the net donor concentration in configuration I is only determined by the concentrations of Si<sup>+</sup> and A<sup>-</sup>, as long as the concentration of T<sup>-</sup> is above  $\sim 10^{17}$  cm<sup>-3</sup>. This represents a more stable configuration, particularly for concentration fluctuation of  $T^-$ , which do not affect the net donor concentration . However, the most crucial aspect is the precise compensation of the electrons, provided by the Si impurity band, from  $\sim 10^{20} \text{ cm}^{-3}$  down to  $\sim 10^{17} \text{ cm}^{-3}$ . Nevertheless, this can reasonably be explained by a self-compensation mechanism, which promotes the formation of native acceptors as the Fermi-level approaches the conduction band. This concurs with several ab-initio studies, claiming that Al vacancies (and their related complexes) play an important role for n-type compensation. [3, 11, 16, 34–38, 103]. Evidence for the enhanced formation of Al vacancies is also in perfect agreement with our luminescence investigations, discussed in chapter 4. The residual, uncompensated electrons are captured by different acceptor-like traps  $(T^-)$  between 500 meV and 860 meV below the conduction band. The uppermost trap, which is occupied with electrons, determines the position of the Fermi-level. Therefore, minor concentration fluctuations the traps explain the shift of the Fermi level, as observed in the admittance measurements, while the net-donor concentration remains almost constant.

In conclusion, the main compensation mechanism in our n-type bulk crystals is due to the formation of Al-vacancies and their related complexes. The doping efficiency is further reduced by the presence of acceptor-like electron traps in the upper half of the bandgap, which pin the Fermi level about 500 – 650 meV below the conduction band. Similar electron traps have been identified in MOCVD grown AlN, which might also explain the widely scattered activation energies for silicon doped AlN found in literature [18, 20, 21, 122–124]. Despite its substantial concentration, we further propose that carbon  $C_N$ , which is also incorporating as a deep acceptor in the lower half of the bandgap [113], is not the main acceptor in our n-type crystals. This is due justified by the fact that a compensation down to precise balance of  $N_D - N_A \approx 1/1000$  is extremely unlikely to occur multiple times in the same manner by extrinsic acceptors. Instead, it is much more likely, that in case carbon is the main acceptor, the crystal becomes insulating.

#### Stable Si<sub>AI</sub> donor model

We identified a DX-like trap in bulk and epitaxial AlN. However, it is unlikely, that this trap is related to silicon impurities. Typically, n-type AlN reveals thermal activation energies below 300 meV [13, 18, 21], which considerably smaller than the 500 meV for the DX-like center. Another metastable center, with an appropriate thermal activation energy comparable to that of AlN:Si, could neither be identified in bulk nor in epitaxial AlN. Therefore, we will propose an alternative model, including a stable Si donor, which is also in perfect agreement with all experimental observations, i.e. the PPC effect (see Fig. 5.22) and the properties of the Si related EPR signal (see Fig. 5.13). According to our conductivity model, Si is forming an impurity band around 110 meV below the conduction band, while the Fermi level is pinned at electron traps, around about 520 - 650 meV below the conduction band. The steady-state condition at low temperatures, i.e. 7 K, is depicted in Fig. 5.22(a). Due to full compensation, the Si donor (impurity band) is positively charged, which explains the absence of an Si-related EPR signal while cooling down the sample in the dark. The  $DX^{-}$  level, where the Fermi level is pinned, is partly occupied with electrons, leaving shallow, positively charged d<sup>+</sup> states in resonance with the conduction band. Among the numerous traps, we only included the DX-like electron trap (TL peak  $A_2$ ) for the sake of clarity.

The PPC and the EPR signal is initiated by optical excitation of two electrons from the deep,  $DX^-$  level into the conduction band (see Fig. 5.31(b)). At low temperatures, the d<sup>+</sup> level can easily be occupied by free electrons, which results in the neutral, metastable d<sup>0</sup> state (also taken to be in resonance with the conduction band). Additionally, the free electrons may occupy the Si donors (impurity band), which therefore becomes neutrally charged, i.e. Si<sup>0</sup><sub>A1</sub>. This paramagnetic state causes the observed EPR signal. Also, in this condition several factors contribute to an increased electrical conductivity: (i) The electrons from the shallow, d<sup>0</sup> configuration, which are in resonance with conduction band and (ii) hopping conductivity in the silicon impurity band. This increased conductivity persists due to the fact that the reconfiguration into the  $DX^-$  state is prevented by a thermal capture barrier.

At about 60 K, the silicon donor band is fully ionized, as drafted in Fig. 5.31(c) and accordingly the EPR signal decreases. However, due to a thermal capture barrier for electrons, the capture rate of the DX<sup>-</sup> configuration is almost negligible and therefore, the decrease of the conductivity is small (see Fig. 5.31(d)). At elevated temperatures, the capture rate successively increases, which explains the minor decrease of the conductivity between 60 K to about 120 K. Above 120 K, the thermal emission of electrons from the DX<sup>-</sup> state is prevailing over the capture rate, which results in an increase of the conductivity. Above 180 K, the thermal emission of electron from the DX<sup>-</sup> state becomes

sufficiently large and photoexcitation does no longer result in an increased conductivity. This is the point where the curves of the cooling and the heating cycle intersect.



Figure 5.31.: Alternative model assuming a stable  $Si_{Al}$  donor and an acceptor like trap in the upper half of the bandgap with a thermal capture barrier. (a) Thermal equilibrium at T~ 10 K. (b) Optical excitation at T~ 10 K causing photoexcitation and subsequent occupation of the  $Si_{Al}$  donor band with electrons. (c) Thermal activation of the  $Si_{Al}$ impurity band around 60 K. The thermal capture barrier of the traps prevents an instant recapture of the electrons. (d) Capture of the free carriers by the deep level 'T' for T > 120 K.

In conclusion, we propose that Si is a stable, shallow donor in AlN with a thermal activation energy of around 150 meV (point defect). We can explain all metastable properties of our n-type AlN crystals with the presence of an unknown, DX-like electron trap, about 500 meV below the conduction band.

Noticeably, the PPC curve in Fig. 5.22 is almost identical to the one presented in Ref. [13], although their proposed n-type conductivity model is entirely different. It is based on a metastable Si-DX center, which pins the Fermi-level about 320 meV below the conduction band. However, we rather suspect, that the same unknown electron trap has been incorporated in their samples, which causes the PPC effect. As we have seen in TL curves from epitaxial AlN,  $A_2$  is commonly present in such samples.

# 6. Summary

The optical properties and trap levels in bulk and epitaxial AlN have been investigated. The most important results are summarized as follows:

- A bound exciton, peaking at 6.012 eV, indicates the presence of a donor with a thermal activation energies of 60 meV, as determined by using Haynes rule. The presence of such a shallow donor state is corroborated by luminescence investigations in the near UV region. This value is considerably below the activation energies for Si on Al site, suggesting that there might be an alternative, even more suitable n-type dopant than Si.
- A bound exciton at 6.006 eV might be related to Si on Al site. The thermal activation energy of the underlying donor, as determined by Haynes rule, is in good agreement with the 110 meV for  $Si_{Al}$  from thermoluminescence curve analysis.
- The acceptor species, involved in a luminescence band around 3.2 eV, is related to Al vacancies. The position of this acceptor, in the triply negatively charged state, is about 2 eV above the valence band. This luminescence band might be useful for studying n-type compensation centers for the optimization of doping.
- For the characterization of traps in AlN, we developed and established thermoluminescence measurements for application in a scanning electron microscope. By choosing appropriate electron beam settings, this enables spatially resolved defect analysis in the range of a few μm. Using this method allowed to record almost completely separable thermoluminescence peaks, which allows a very accurate determination of the trap parameters.
- Thermoluminescence investigation on n-type AlN, reveled that Si incorporates as a stable, shallow donor, about 110 150 meV below the conduction band (depending on the concentration). Evidence for a Si related DX transition have not been found.
- By thermoluminescence measurements, we identified at least eight electron traps, with three of them, about 520 meV, 625 meV and 860 meV below the conduction band, occurring in substantial concentrations. These three electron traps have also been characterized by stationary, electrical methods, showing very good agreement with results from thermoluminescence curve fitting.

- A detailed model for the n-type conductivity and the main compensation centers has been developed. The n-type conductivity is due to Si, incorporating on Al site. As compensation centers, we found that self compensation (Al vacancies and their related complexes) is the most important mechanism in the lower half of the bandgap. Carbon, incorporating on N site, also counteracts on n-type doping but it is however not the main acceptor in our n-type crystals. In addition, the n-conductivity is further impaired by the presence of deep, acceptor-like traps about 520 meV, 625 meV and 860 meV below the conduction band. These traps cause Fermi-level pinning and thus severely reduce the free electron concentration at room temperature. Since they could also be identified in several epitaxial AlN samples, this suggesting that they might impair the electrical properties in the same manner. The unintended incorporation of such traps might also explain the varying thermal activation energies for silicon doped AlN found in literature. A reduction of these electron traps is therefore a prerequisite for improving the n-conductivity in AlN.
- We identified an unknown electron trap, about 520 meV below the conduction band, which possessed DX-like characteristics. The thermal capture barrier for electrons is coarsely 70 meV. This trap causes persistent photo-conductivity and influences the optical properties, by acting as a competitive, non-radiative recombination center. We consider it unlikely that this trap is related to O or Si impurities. This trap has also been identified in several epitaxial AlN samples, suggesting that it might influence the electrical and optical properties in the same manner.

## A. Appendix

### A.1. Thermoluminescence curve analysis

### A.1.1. Numerical curve fitting

In the following, some of the effects on TL curves, caused by variations of the parameters, shall be demonstrated. In Fig. A.1 the ratio of the capture coefficients for the electron trap 'T' and the recombination center 'R', i.e.  $c_n^T / c_n^R$ , has been varied for a defect with E = 0.5 eV,  $s = 1 \times 10^{10} \text{s}^{-1}$  using a linear heating rate of  $\beta = 0.15 \text{ K/s}$ . If  $c_n^T / c_n^R \gg 1$ , the curve takes on Gaussian-like shape and the peak is shifted to higher temperatures. If  $c_n^T / c_n^R \ll 1$  the peak becomes increasingly asymmetric due to a steeper high temperature side. The physical origin of this effect is that the ratio  $c_n^T / c_n^R$  affects the probability of electron re-trapping into 'T' during the TL emission. Large values induce strong, whereas low values cause small re-trapping.



Figure A.1.: Calculated TL curves for different ratios of  $c_n^T$  and  $c_n^R$ .

A similar effect can be caused by varying the initial trap filling ratio i.e.  $n^T/N^T$ . For this simulation all other parameters were kept constant, i.e. E = 0.5 eV,  $s = 1 \times 10^{10} \text{s}^{-1}$ ,  $N^R = N^T = \text{const}$  and  $c_n^T = c_p^R = 1 \cdot 10^{-10} \text{cm}^3 \text{s}^{-1}$ . The simulated curves are displayed in Fig.A.2. In case  $n^T/N^T \ll 1$ , the TL peak becomes broader and is shifted to higher temperatures. This effect is also originating from the increased re-trapping due to a larger number of unoccupied traps.



Figure A.2.: Calculated TL curves for different ratios of  $n^T/N^T$ .

### A.1.2. Analytical curve fitting

For the analytical curve fit, the following approximation are applied to Eq. (2.3). First, one assumes that the number of electrons in the conduction band is only slowly varying, compared to the population of the trap 'R' or the recombination center 'R'. This means that,

$$|\frac{dn}{dt}| \ll |\frac{dn^T}{dt}|, |\frac{dp^R}{dt}|$$

Under this condition

$$-\frac{dn^T}{dt} \approx -\frac{dp^R}{dt} \propto \mathbf{I}_{\mathrm{TI}}$$

This simplifies Eq. (2.3) to

$$I_{TL} = \frac{-N^R c_n^R (1 - f^R) \cdot N^T e_n^T f^T}{N^T c_n^T (1 - f^T) + N^R c_n^R (1 - f^R)}$$
(A.1.1)

Second, the treatment of charge carrier re-trapping is simplified. In the model of Randal and Wilkins [125, 126] re-trapping of charge carriers is neglected, i.e.  $c_n^R(1 - f^R) \gg c_n^T(1 - f^T)$ . This gives the so called 'first-order' model

$$\frac{dp^R}{dt} = n^T \cdot e_n^T = n^T s \exp(-\frac{E}{kT})$$
(A.1.2)

The opposite case was considered by Garlick and Gibson [127], i.e.  $c_n^R(1 - f^R) \ll c_n^T(1 - f^T)$  with the additional assumption of  $n^T \ll N^T$  and  $n^T = p^R$ . This leads to the

'second order' model

$$\frac{dp^R}{dt} = (n^T)^2 s' \exp(-\frac{E}{kT}) \tag{A.1.3}$$

If none of the above models applies to the experimental curves, the general order model, introduced by May and Partridge can be used instead [89].

$$\frac{dp^R}{dt} = (n^T)^b s' \exp(-\frac{E}{kT}) \tag{A.1.4}$$

Hereby, the frequency factor s has been replaced by  $s' = sc_n^R/(N^T c_n^T)$ . The general order expression contains the additional parameter b, which allows to vary the kinetic order from weak ( $b \approx 1$ ) to strong ( $b \approx 2$ ) re-trapping. Integration of Eq.(A.1.4), using a linear heating rate of  $\beta$  [K/s] leads to the expression

$$I_{TL} = n_0^T s'' \exp\left(-\frac{E}{kT}\right) \left[1 + \left((b-1)\frac{s''}{\beta}\right) \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-\frac{b}{b-1}}$$
(A.1.5)

with  $s'' = s'(n_0^T)^{b-1}$ .

The 'general order model' has the advantage that both, the 'first' as well as the 'second order model' can easily be reproduced by varying the *b* parameter. This effect is demonstrated in Fig. A.3. For  $b \rightarrow 2$  the TL peak takes on a Gaussian shape, whereas if  $b \rightarrow 1$ , the TL curve becomes asymmetric, as for the 'first-order' case.



Figure A.3.: Effect of the re-trapping factor b on the TL curve.

# Lebenslauf

Name:	Tobias Schulz		
Geburtsdatum:	01.09.1974		
Geburtsort:	Hanau am Main		
1982 - 1986	Erich Kästner Grundschule in Hanau		
1986 - 1988	Otto Hahn Schule in Hanau		
1988 - 1995	Hohe Landesschule Hanau		
1995 - 1996	Zivildienst bei der Selbsthilfe Körperbehinderter e.V. in Erlensee.		
1996 - 2002	Justus Liebig Universität in Gießen mit der Fachkombination Physik / Spor		
	1. Staatsexamensarbeit bei Prof. Dr. Meyer am 1. Physikalischen Institut.		
	Thema der Arbeit: "Rekombinationsmechanismen in GaN und ZnO".		
2002 - 2005	Siemens AG Berlin / Technische Universität Berlin. BMBF Projekt "Mecha-		
	tronik".		
2005 -	Leibniz-Institut für Kristallzüchtung		

## Literaturverzeichnis

- E. Silveira, J.A. Freitas, G.A. Slack, and L.J. Schowalter. *Phys. stat. sol (c)*, 0:2618, 2003.
- [2] E. Silveira, J.A. Freitas, S.B. Schujman, and L.J. Schowalter. Journal of Crystal Growth, 310:4007, 2008.
- [3] A. Fara, F. Bernardini, and V. Fiorentini. J. Appl. Phys, 85:2001, 1999.
- [4] Y. Taniyasu, M. Kasu, and T.Makimoto. Appl. Phys. Lett, 85:4672, 2004.
- [5] T. Ive, O. Brandt, H. Kostial, K. J. Friedland, L. Däweritz, and Klaus H. Ploog. Appl. Phys. Lett, 86:024106, 2005.
- [6] Y. Taniyasu, M. Kasu, and T. Makimoto. *Nature*, 441:325, 2006.
- [7] S.B. Zhang, S.H. Wei, and A. Zunger. Phys. Rev. Lett., 84:1232, 2000.
- [8] M. Mizuta, M. Tachikawa, H. Kukimoto, and Shigeru Minomura1. Jpn. J. Appl. Phys., 24:L143, 1985.
- [9] P. M. Mooney. J. Appl. Phys., 67:R1, 1990.
- [10] P. Boguslawski and J. Bernholc. Phys. Rev. B, 56:9496, 1997.
- [11] T. Mattila and R.M. Nieminen. Phys. Rev. B, 54:16676, 1996.
- [12] C.H. Park and D.J.Chadi. Phys. Rev. B, 55:12995, 1997.
- [13] R. Zeisel, M.W. Bayerl, S.T.B. Goennerwein, R. Dimitrov, O. Ambacher, M.S. Brandt, and M.Stutzmann. *Phys. Rev. B*, 61:R16283, 2000.
- [14] C.Skierbiszewski, T.Suski, M.Leszczynski, M. Shin, M.Skowronski, M.D. Bremser, and R.F.Davis. Appl. Phys. Lett., 74:3833, 1999.
- [15] C.G. Van de Walle. *Phys. rev. B*, 57:R2033, 1998.
- [16] C. Stampfl and C. G. Van de Walle. *Phys. Rev. B*, 65:155212, 2002.
- [17] L.E. Ramos, J.Furthmller, J.R.Leite, L.M.R. Scolfaro, and F. Bechstedt. Phys. Rev. B, 68:085209, 2003.

- [18] M. L. Nakarmi, K. H. Kim, K. Zhu, J. Y. Lin, and H. X. Jiang. Appl. Phys. Lett., 85:3769, 2004.
- [19] M. D. McCluskey, N. M. Johnson, C. G. Van de Walle, D. P. Bour, M. Kneissl, and W. Walukiewicz. *Phys. Rev. Lett.*, 80:4008, 1998.
- [20] Y. Taniyasu, M. Kasu, and N. Kobayahsi. Appl. Phys. Lett, 81:1255, 2002.
- [21] Y.Taniyasu and M. Kasu. Diamond and Rel. Materials, 17:1273, 2008.
- [22] K.B. Nam, M.L. Nakarmi, J.Y. Lin, and H.X. Jiang. Appl. Phys. Lett., 82:1694, 2003.
- [23] E. Silveira, J.A. Freitas, O.J. Glembocki, G.A. Slack, and L.J. Schowalter. Phys. Rev. B, 71:041201, 2005.
- [24] E. Silveira, J.A. Freitas, M. Kneissel, D.W. Treat, N.M. Johnson, G.A. Slack, and L.J. Schowalter. Appl. Phys. Lett., 84:3501, 2004.
- [25] Y. Yamada, K. Choi, S. Shin, H. Murotani, T. Taguchi, N. Okada, and H. Amano. Appl. Phys. Lett., 92:131912, 2008.
- [26] N. Nepal, J.Li, M.L.Nakarmi, J.Y. Lin, and H.X.Jiang. Appl. Phys. Lett., 88:062103, 2006.
- [27] G.M. Prinz, A. Ladenburger, M. Feneberg, M. Schirra, S.B. Thapa, M. Bickermann, B.M. Epelbaumc, F. Scholz, K. Thonke, and R. Sauer. *Superlattices and Microstructures*, 40:513, 2006.
- [28] E. Kuokstis, J. Zhang, Q. Fareed, J. W. Yang, G. Simin, M. Asif Khan, R. Gaska, M. Shur, C. Rojo, and L. Schowalter. *Appl. Phys. Lett.*, 81:2755, 2002.
- [29] L. Chen, B. J. Skromme, R. F. Dalmau, R. Schlesser, Z. Sitar, C. Chen, W. Sun, J. Yang, M. A. Khan, M. L. Nakarmi, J. Y. Lin, and H.-X. Jiang. Appl. Phys. Lett., 85:4334, 2004.
- [30] J. Rosa and I.Tale. Czech. J. Phys, 29:810, 1979.
- [31] I. Tale and J. Rosa. *Phys. stat. sol.* (a), 86:319, 1984.
- [32] H. Gobrecht and D. Hofmann. J. of Pysics and Chem. of Solids, 27:509, 1966.
- [33] W. A. Groen, J. G. van Lierop, and A. Roosen. J. Mater. Sci. Lett., 12:1224.
- [34] T. Mattila and R.M. Nieminen. *Phys. Rev. B*, 55:9571, 1997.

- [35] I. Gorczyca, N. E. Christensen, and A. Svane. Phys. Rev. B., 66:075210, 2002.
- [36] K. Laaksonen, M. G. Ganchenkova, and R M Nieminen. J. Phys.: Condens. Matter, 21:015803, 2009.
- [37] Y. Zhang, W. Liu, and H. Niu. Phys. Rev. B, 77:035201, 2008.
- [38] P. Boguslawski, E.L. Briggs, and J. Bernholc. Phys. Rev. B, 51:17255, 1995.
- [39] N. Nepal. Deep ultraviolet photoluminescence studies of Al-rich AlGaN and AlN epilayers and nanostructures. PhD thesis, Kansas State University Manhattan, Kansas, 2006.
- [40] K.B. Nam, M.L. Nakarmi, J.Y. Lin, and H.X. Jiang. Appl. Phys. Lett., 86:222108, 2005.
- [41] A. Dadgar, A. Krost, J. Christen, B. Bastek, F. Bertram, A.Krtschil, T. Hempel, J. Bläsing, U. Haboeck, and A. Hoffmann. J. Cryst. Growth, 297:306, 2006.
- [42] B. Bastek, F.Bertram, J. Christen, T. Hempel, A. Dadgar, and A. Krost. Appl. Phys. Lett., 95:032106, 2009.
- [43] R. Freitag, K. Thonke, R. Sauer, D. G. Ebling, and L. Steinke. MRS Internet J. Nit. Sem. Res., 10:3, 2005.
- [44] M.Bickermannm, B.M. Epelbaum, and A. Winnacker. J. Cryst. Growth, 269:432, 2004.
- [45] M.Bickermannm, B.M. Epelbaum, M. Kazan, Z.Harro, P. Masri, and A. Winnacker. Phys. stat. sol. (a), 202:531, 2005.
- [46] J. A. Freitas. J. Ceram. Proc. Res., 6:209, 2005.
- [47] G.A. Slack, L.J.Schowalter, D.Morelli, and J.A. Freitas Jr. J. Cryst. Growth, 246:287, 2002.
- [48] M. Strassburg, J. Senawiratne, N. Dietz, U.Haboeck, A. Hoffmann, V.Noveski, R. Dalmau, R. Schlesser, and Z. Sitar. J. Appl. Phys., 96:5870, 2004.
- [49] G.H. Wannier. *Phys. Rev.*, 52:191, 1937.
- [50] W. Kohn. Solid state physics V. Academic press, Inc, New York, USA, 1957.
- [51] A. S. Barker, Jr., and M. Ilegems. *Phys. Rev. B*, 7:743, 1973.

- [52] M. Drechsler, D. M. Hofmann, B. K. Meyer, T. Detchprohm, H. Amano, and I. Akasaki. Jpn. J. Appl. Phys, Part 2, 34:L1178, 1995.
- [53] H. Wang and A.B. Chen. J. Appl. Phys., 7:7859, 2000.
- [54] W.J. Moore, J.A. Freitas, R.T. Holm, O.Kovalenkov, and V. Dmitriev. Appl. Phys. Lett., 86:141912, 2005.
- [55] P. Rinke, M. Winkelnkemper, A. Qteish, D. Bimberg, J. Neugebauer, and M. Scheffler. Phys. Rev. B, 77:075202, 2008.
- [56] D.V. Lang and R.A. Logan. Phys. Rev. Lett, 39:635, 1977.
- [57] D.V. Lang, R.A. Logan, and M. Jaros. Phys. Rev. B, 19:1015, 1979.
- [58] D.J.Chadi and K.J.Chang. Phys. Rev. Lett, 61:873, 1988.
- [59] F. Seitz. Z. Physik, 101:680, 1936.
- [60] E.U. Condon and P.M. Morse. Quantum Mechanics. McGraw Hill, USA ,N.Y., 1929.
- [61] N.F.Mott. Trans. Faraday Soc., 34:500, 1938.
- [62] J.R.Haynes. Phys. Rev. Lett., 4:361, 1960.
- [63] B.K. Meyer. Mater. Res. Soc. Symp. Proc., 449:479, 1997.
- [64] K. Huang and A. Rhys. Proc. Roy. Soc., A204:406, 1950.
- [65] B. Henderson and G.F. Imbusch. Optical spectroscopy of inorganic solids. Oxford, Oxford, GBR, 1988.
- [66] C. C. Klick and J. H. Schulman. Solid State Phys, 5:97, 1957.
- [67] K. Colbow. Phys. Rev., 141:742, 1966.
- [68] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak. Phys. Rev., 140:A202, 1965.
- [69] T. Schmidt, K. Lischka, and W. Zulehner. Phys. Rev. B, 45:8989, 1992.
- [70] M. A. Reshchikov, G.C. Yi, and B.W. Wessels. Phys. Rev. B, 59:13176, 1999.
- [71] B. I. Shklovskii and A. L. Efros. *Electronic Properties of Doped Semiconductors*. Springer, Berlin, GER, 1984.

- [72] S.W.S. McKeever, J.F. Rhodes, V.K. Mathur, R. Chen, M.D. Brown, and R.K. Bull. *Phys. Rev. B*, 32:3835, 1985.
- [73] P.J. Kelly and P.Bräunlich. Phys. Rev., B1:1587, 1970.
- [74] R.K. Bull, S.W.S McKeever, R. Chen, V.K. Mathur, Joanne F. Rhodes, and M.D. Brown. J. Phys D: Appl. Phys., 19:1321, 1985.
- [75] R. Visocekas, T. Ceva, D. Lapraz, P. Iacconi, and F. Lefaucheux. Phys. stat. sol (a), 15:61, 1973.
- [76] J.P. Ponpon and R. Stuck. Semicond. Sci. Technol., 14:331, 1999.
- [77] W. Shockley and W.T. Read. Phys. Rev., 87:835, 1952.
- [78] R.N. Hall. Phys. Rev., 87:387, 1952.
- [79] R.Chen, S.W.S. McKeever, and S.A. Durrani. Phys. Rev. B, 24:4931, 1981.
- [80] D.E. Newbury, D.B. Holt, and D.C. Joy. SEM characterization of semiconductors. Academic Press, London, GBR, 1981.
- [81] D.C. Joy and S. Luo. *Scanning*, 11:176, 1989.
- [82] H. Bethe. Ann. Phys., 397:325, 1930.
- [83] D. Drouin, P. Hovington P, and R. Gauvin. Scanning, 19:20, 1997.
- [84] D. Drouin, A. R. Couture, D. Joly, X. Tastet, V. Aimez, and R. Gauvin. Scanning, 29:92, 2007.
- [85] W. Ehrenberg and D.J. Gibbons. Electron Bombardment Induced Conductivity and Its Applications. Academic Press, London, GBR, 1981.
- [86] A. Lastras-Martinez. J. Appl. Phys., 50:4156, 1979.
- [87] T. Stiasny and R.Helbig. J. Appl. Phys, 79:4152, 1996.
- [88] A.Halperin and A.A.Braner. Phys Rev., 117:408, 1960.
- [89] C.E.May and J.A. Partridge. J. Chem. Phys., 40:1401, 1964.
- [90] G.P. Summers. Rad. Prot. Dos., 8:69, 1984.
- [91] D.L.Losee. J. Appl. Phys., 46:2204, 1975.
- [92] D. V. Lang. J. Appl. Phys., 45:3023, 1974.

- [93] J.L. Pautrat, B. Katircioglu, N. Magnea, D. Bensahel, J.C. Pfister, and L. Revoil. Sol. Stat. Electron., 23:1159, 1980.
- [94] C. Hartmann, J. Wollweber, Seitz C, M. Albrecht, and R. Fornari. J. of Cryst. Growth, 310:930, 2008.
- [95] K. Kornitzer, W. Limmer, K. Thonke, R. Sauer, D.G. Ebling, L.Steinke, and K.W.Benz. J. Cryst. Growth, 201/202:441, 1999.
- [96] B. Monemar, P.P. Paskov, J.P. Bergman, M. Iwaya, S. Kamiyama, H. Amano, and I. Akasaki. *Physica B*, 376-377:460, 2006.
- [97] S. O. Kucheyev, M. Toth, M. R. Phillips, J. S. Williams, and C. Jagadish. Appl. Phys. Lett., 79:2154, 2001.
- [98] M.A. Reshchikov, V. Avrutin, N. Izyumskay, R. Shimad, and H. Morkoc. *Physica B*, 401-402:374, 2007.
- [99] M. A. Reshchikov, F. Shahedipour, R. Y. Korotkov, M. P. Ulmer, and B. W. Wessels. *Physica B*, 273-274:105, 1999.
- [100] F. Karel and J. Pastrnak. Czech. J. Phys., 20:46, 1970.
- [101] R. Pässler, E. Griebl, H. Riepl, G. Lautner, S. Bauer, H. Preis, W. Gebhardt, B. Buda, D.J. As, D. Schikora, K. Lischka, K. Papagelis, and S. Ves. J. Appl. Phys., 86:4403, 1999.
- [102] J.W. Steeds, G.A. Evans, L.R. Danks, S. Furkert, W. Voegeli, M.M. Ismail, and F. Carosella. *Diamond Relat. Mater.*, 11:1923, 2002.
- [103] J. Slotte, F. Tuomisto, K. Saarinen, C.G. Moe, S. Keller, and S.P. DenBaars. Appl. Phys. Lett., 90:151908, 2007.
- [104] N. Nepal, K.B. Nam, M.L. Nakarmi, J.Y. Lin, H.X. Jiang, J.M. Zavada, and R.G. Wilson. Appl. Phys. Lett., 84:1090, 2004.
- [105] Q. Zhou and M.O. Manasreha. Appl. Phys. Lett., 80:2072, 2002.
- [106] T. Suski, P. Perlin, H. Teisseyre, M. Leszczyski, I. Grzegory, J. Jun, M. Bokowski, S. Porowski, and T. D. Moustakas. *Appl. Phys. Lett.*, 67:2188, 1995.
- [107] P. Perlin, T. Suski, H. Teisseyre, M. Leszczynï£ · ski, I. Grzegory, J. Jun, S.Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian, and T.D. Moustakas. *Phys. Rev. Lett.*, 75:296, 1995.

- [108] P. Perlin, T. Suski, A. Polian, J. C. Chervin, W. Knap, J. Camassel, I. Grzegory, S. Porowski, and J. W. Erickson. *Mater. Res. Soc. Symp. Proc.*, 449:519, 1997.
- [109] C. Wetzel, T.Suski, J.W. Ager, E.R. Weber, E.E.Haller, S. Fischer, B.K.Meyer, R.J.Molnar, and P.Perlin. *Phys. Rev. Lett.*, 78:3923, 1997.
- [110] C. Wetzel, W. Walukiewicz, E. E. Haller, J. W. Ager III, I. Grzegory, S. Porowski, and T. Suski. *Phys. Rev. B*, 53:1322, 1996.
- [111] N. Nepal, M. L. Nakarmi, J. Y. Lin, and H. X. Jiang. Appl. Phys. Lett., 89:092107, 2006.
- [112] P. Lu, R. Collazo, R. F. Dalmau, G. Durkaya, N. Dietz, and Z. Sitar. Appl. Phys. Lett, 93:131922, 2008.
- [113] L.E. Ramos, J. Furthmller, L.M.R. Scolfaro, J.R. Leite, and F. Bechstedt. Phys. Rev. B, 66:075209, 2002.
- [114] W. E. Carlos, J. A. Freitas, M. Asif Khan, D. T. Olson, and J. N. Kuznia. Electronspin-resonance studies of donors in wurtzite gan. *Phys. Rev. B*, 48(24):17878, 1993.
- [115] M.Benabdesselam, P.Iacconi, D.Lapraz, P.Grosseau, and B. Guilhot. J. Phys. Chem., 99:10319, 1995.
- [116] F. Porte, J.P. Lecompte, J. Jarrige, A.Collange, P.Grosseau, and B.Guilhot. J. of European Cerm. Soc., 17:1797, 1997.
- [117] H. G. Lee, M. Gershenzon, and B. L. Goldenberg. J. Electron. Mater., 20:621, 1991.
- [118] I. Vurgaftman, J. R. Meyer, and L. R. Ram-Mohan. J. Appl. Phys., 89:5815, 2001.
- [119] P. M. Mason, H. Przybylinska, G. D. Watkins, W. J. Choyke, and G. A. Slack. *Phys. Rev. B*, 59:1937, 1999.
- [120] E. Monroy, J. Zenneck, G. Cherkashinin, O. AMbacher, M.Hermann, M. Stutzmann, and M. Eickhoff. Appl. Phys. Lett., 88:71906, 2006.
- [121] A. Sedhain, L. Du, J. H. Edgar, J. Y. Lin, and H. X. Jiang1. Appl. Phys. Lett., 95:262104, 2009.
- [122] B. Borisov, V.Kuryatov, Yu. Kudryavtsev, R. Asomoza, S. Nikishin, D.Y. Song, M. Holtz, and H. Temkin. Appl. Phys. Lett., 87:132106, 2005.

- [123] M. Hermann, F.Furtmayr, A. Bergmaier, G. Dollinger, M.Stutzmann, and M.Eikhoff. Appl. Phys. Lett, 86:192108, 2005.
- [124] R.Boger, M.Fiederle, L.Kirste, M.Maier, and J.Wagner. J. Phys. D:Appl. Phys, 39:4616, 2006.
- [125] J.T. Randall and M.H.F. Wilkins. Proc. Roy. Soc. London, 184:366, 1945.
- [126] J.T. Randall and M.H.F. Wilkins. Proc. Roy. Soc. London, 184:390, 1945.
- [127] G.F. Garlick and A.F. Gibson. Proc. Roy. Soc. London, A60:574, 1948.