DEPARTAMENTO DE INGENIERÍA ELECTRÓNICA

ESCUELA TÉCNICA SUPERIOR DE INGENIEROS DE
TELECOMUNICACIÓN

UNIVERSIDAD POLITÉCNICA DE MADRID

TESIS DOCTORAL

**Deep levels and acceptors in Zn(Mg)O: effect of
N-doping**

Autor: Alejandro Kurtz de Griño

*Ingeniero Técnico Industrial, especialidad en Electrónica Industrial
Ingeniero de Telecomunicación*

Director: Dr. Adrián Hierro Cano

Profesor Titular de Universidad

2017

Tesis Doctoral: **Deep levels and acceptors in Zn(Mg)O: effect of N-doping**

Autor: Alejandro Kurtz de Griñó

Director: Dr. Adrián Hierro Cano

El tribunal nombrado por el Mgfco. y Excmo. Sr. Rector de la Universidad Politécnica de Madrid, el día ... de de 201....., para juzgar la Tesis arriba indicada, compuesto por los siguientes doctores:

Dr.....(PRESIDENTE)

Dr.....(VOCAL)

Dr.....(VOCAL)

Dr.....(VOCAL)

Dr.....(SECRETARIO)

Realizado el acto de lectura y defensa de la Tesis el día de de 201..... en acuerda otorgarle la calificación de:

El presidente:

El secretario:

Los vocales:

Abstract

Versión española

Esta tesis pretende analizar el efecto del dopado de capas gruesas de ZnO y MgZnO dopadas con N y sin dopar, mediante técnicas de espectroscopía de niveles profundos. La elección del material vino motivada por su posible competición al GaN, que actualmente domina el mercado de iluminación semiconductor. Para ello, sería necesario extender el ZnO a dispositivos bipolares, mediante el dopado tipo p, que actualmente resulta imposible de conseguir de una manera repetible.

El documento se divide en cuatro partes principales, estando la primera dedicada a la exposición de los conceptos teóricos subyacentes a la temática de la tesis, así como a las técnicas experimentales utilizadas para la obtención de los resultados científicos. En el segundo bloque, se describen los desarrollos realizados en los equipos de caracterización, que han sido objeto de un fuerte trabajo durante la duración de la tesis. La técnica desarrollada para extender las medidas de espectroscopía basada en capacidad a dispositivos metal-aislante-semiconductor (MIS en sus siglas inglesas) completa esta parte, siendo este estudio aplicable a otros materiales aparte del ZnO.

Durante el tercer bloque se describen los principales resultados experimentales obtenidos en dispositivos Schottky/MIS, que asimismo pueden ser nuevamente divididos en dos grandes secciones, ambas dedicadas al objetivo de conseguir material tipo p mediante el dopaje con N. El primer acercamiento al problema pretende obtener dicha conductividad mediante la obtención del material con la mejor calidad cristalina posible, reduciendo el número de defectos eléctricamente activos tanto cerca de la banda de conducción como de valencia, minimizando en lo posible el comportamiento tipo n, intrínseco a este material.

Para ello, se analizaron previamente tres muestras crecidas homoepitaxialmente mediante epitaxia de haces moleculares en dos orientaciones no polares (a- y m-) y una semipolar (r-), que en estudios anteriores han mostrado la mejor calidad cristalina. En ellos se analizaron los niveles energéticos tanto cerca de la banda de conducción como de la banda de valencia, obteniendo un menor valor de concentración para todos ellos en la orientación m-. Un nuevo nivel muy cercano a la banda de conducción, posiblemente relacionado con el H, fue medido mediante DLTS, lo que supone el nivel menos profundo obtenido hasta la fecha en ZnO mediante técnicas eléctricas. En el estudio realizado en material crecido en plano m- dopado con N se analizaron los niveles aceptores presentes en el material, obteniendo una relación entre la compensación mostrada por los dispositivos y la concentración del dopante. Además de los niveles intrínsecos debidos a la vacante de zinc, se obtuvieron dos nuevos niveles aceptores relacionados con la inclusión de N, uno de ellos coincidente con la energía del aceptor responsable del DAP obtenido en medidas de fotoluminiscencia a baja temperatura, si bien ello no condujo a un comportamiento tipo p en este material.

El otro camino para la obtención de dicha conductividad se realizó en material con una determinada composición de Mg, crecida por MOCVD y con concentraciones crecientes de N. Nuevamente, en el análisis de los dispositivos se obtuvieron una serie de niveles cuya concentración escala perfectamente con la exposición al flujo de N, siendo el menos profundo de estos aceptores coincidente con uno de los obtenidos en el estudio anterior. La presencia de una capa aislante en la superficie convierte a los dispositivos en MIS, lo que unido a la alta compensación presente en el material, lleva a una alta variación en la capacidad medida respecto al valor de oscuridad en estado estacionario. Ello obligó al cálculo de las concentraciones mediante medidas de capacidad-voltaje bajo iluminación, de las cuales mediante el modelo de dispositivo MIS aplicado en la capacidad mínima, permitió obtener los valores para algunos de los niveles observados.

Por último, un análisis de muestras implantadas con N no reveló ninguna relación con dicho proceso, a pesar de los resultados existentes en la literatura. Asimismo, dos muestras con diferentes heteroestructuras de ZnO/MgZnO fueron medidas, con el objetivo de procesar dispositivos HEMT, si bien no se encontró evidencia de la capa 2DEG necesaria para el funcionamiento de dichos dispositivos. En cualquier caso, este estudio sirvió para encontrar una serie de tácticas de gran utilidad para un futuro análisis de estructuras multicapa mediante espectroscopía de niveles profundo.

La tesis se completa con un profundo análisis bibliográfico, resumido en una tabla con todos los niveles eléctricamente activos publicados hasta la fecha en revistas de alto impacto, y que sirve para guiar la atribución y comparación de los resultados obtenidos en este y futuros estudios en ZnO.

English version

This thesis analyzes the effect of doping in ZnO and MgZnO layers, both intentionally doped with N and non intentionally doped, by means of deep level spectroscopic techniques. ZnO has been chosen because of its suitability as a substitute for GaN, which dominates the solid state illumination industry. For doing so, ZnO technology must be extended towards bipolar devices, obtaining p-type doping, which is nowadays impossible to reproduce.

The dissertation is divided onto four principal parts. The first one introduces the main theoretical aspects of the material and devices used during the thesis, as well as the characterization techniques used for obtaining the experimental results. The second block describes the improvements that have been performed on the experimental setups, along with the theoretical and practical aspects needed for the measurement of MIS devices by deep level spectroscopy techniques.

The third block explains the principal results obtained in Schottky and MIS devices. This part can be divided on two main paths intended to explain p-type doping in ZnO or the effect of N-doping. The first one focuses on obtaining the best material quality, measuring homoepitaxial material grown in different orientations and choosing the one with the lowest carrier concentration.

For doing so, three samples grown homoepitaxially by MBE in two non-polar orientations (a- and m-) and one semipolar plane (r-) were analyzed. This material has shown previously the best crystalline quality. On these material, devices were processed and the energetic levels both close to the conduction and valence bands were analyzed by DLTS and DLOS, obtaining the lowest residual carrier concentration for the m-plane sample. A new very shallow level close to the conduction band was found, possibly related to H, which is the energy with the lowest energy offset obtained to the date by DLTS in ZnO. Overall, the m-plane sample showed a lower trap density, that tracks the reduction in residual carrier concentration. Therefore, this orientation was chosen as the candidate for p-type doping, obtaining three more samples doped with increasing N concentrations. On them, the compensation observed by basic electrical measurements was analyzed by DLOS, observing new acceptor levels close to the valence band. One of these levels correlates with the DAP observed by photoluminescence, which has been related with a N-related acceptor. However, no p-type behavior was obtained.

The second approach towards p-type conductivity consists in alloying with Mg, at low compositions, which maintains good material quality while reducing the intrinsic carrier concentration. This effect comes both from a reduction in the efficiency of the native donors and compensation by zinc vacancies. Three samples grown by MOCVD were obtained with different N concentrations, which showed an electrical compensation that perfectly tracks the exposure to the N flow. Various acceptor traps were measured by DLOS, one of them coincident with the previously observed N-related DAP acceptor. However, their concentrations had to be measured invoking an MIS model for analyzing the LCV profiles. By doing so, a concentration for many of the levels was calculated and tracked the N concentration.

Finally, a study of layers implanted with N species was performed, without evidence of newly created levels close to the valence band, nor electrical compensation. Another study dedicated to the measurement of HEMT structures was performed on heterostructures, although no indication of a 2DEG layer was obtained. However, some tips for the measurement of multilayered structures were obtained, which can help future studies on these kind of devices.

The document is completed with a thorough bibliographical study, summarized in a table that includes all the existing reports of electrically active defects in ZnO, which can help to guide the attribution and comparison of the measured defects in this and future studies in ZnO.

Contents

Abstract	v
I Introduction and theory	1
Preface	3
1 Introduction	7
1.1 Introduction to ZnO	7
1.1.1 Alloying of ZnO	8
1.2 Defect states in semiconductors - deep levels	9
1.3 Doping of ZnO	11
1.3.1 The role of native defects	13
1.3.2 Intrinsic defects observed by DLTS	17
1.3.3 Towards p-type ZnO: The doping asymmetry & N-doping	19
1.4 Schottky barrier diodes	20
1.4.1 Depletion region in a Schottky barrier	21
1.4.2 Junction capacitance	22
1.5 Metal-insulator-semiconductor diodes	23
1.5.1 Capacitance in MIS devices	27
1.6 Capture-emission kinetics	30
1.6.1 Equilibrium carrier statistics	30
1.6.2 Dynamics of deep states in semiconductors	31
1.7 Space charge transients	33
1.8 Capacitance transients	34
1.9 Optical processes in semiconductors	34
1.9.1 Band-to-band transitions	35
1.9.2 Excitonic transitions	36
1.9.3 Defect-driven transitions	36
1.9.4 Optical parameters of ZnO	36
2 Characterization and processing techniques	37
2.1 Device fabrication	37
2.1.1 Material growth	37
2.1.2 Device processing	37
2.2 Current-Voltage characteristics	39
2.3 Capacitance-Voltage profiling	40
2.3.1 Measurement of a junction capacitance	40
2.3.2 Capacitance-Voltage profiling	44

CONTENTS

2.4	Deep Level Transient Spectroscopy	45
2.4.1	The technique	45
2.4.2	Parameter extraction	50
2.4.3	Operation	52
2.4.4	Parameter choice	54
2.5	Deep Level Optical Spectroscopy	55
2.5.1	Operation	55
2.5.2	Parameter extraction	56
2.5.3	Parameter choice	57
2.6	Lighted Capacitance-Voltage profiling	59
2.7	Photoluminescence	60
II	Equipment and techniques development	63
3	Deep level spectroscopy in Metal-Insulator-Semiconductor devices	65
3.1	Introduction	65
3.2	Theoretical Model	66
3.2.1	Basic MIS theory	66
3.2.2	MIS structures for deep level spectroscopy	68
3.2.3	Simulation of DLTS spectra on MIS structures	71
3.3	DLTS analysis on MIS test structures	74
3.4	Conclusions	77
4	Development and improvements on the deep level spectroscopic setups	79
4.1	New lithography mask: yield improvements	79
4.1.1	The old mask	79
4.1.2	Designing a new mask	80
4.2	The measurement setup as-found	81
4.2.1	Hardware	81
4.2.2	Software	83
4.2.3	Main limitations	84
4.3	Hardware improvements	84
4.3.1	Frequency-dependent measurements: low noise transimpedance amplifier	85
4.3.2	Advanced centering	86
4.3.3	Improvement on acquisition rate: oversampling and filtering	86
4.3.4	Automatic lamp control & water filter temperature monitoring	88
4.4	Software improvements	89
4.4.1	Capacitance values	89
4.4.2	Timing	89
4.4.3	Data saving	90
4.4.4	Custom optical changes	90
4.4.5	Many-RW measurement	90
4.4.6	Fourier DLTS	90
4.4.7	Transient saving	91
4.4.8	Data analysis	91
4.4.9	General software optimization and modernization	93
4.5	The aftermath	95

III	Experimental results	97
5	Deep level analysis of homoepitaxial ZnO in non-polar and semipolar orientations	99
5.1	Introduction	99
5.1.1	Samples description	100
5.1.2	Electrical characterization of the devices	100
5.2	Optical differences between non-polar and semipolar ZnO	101
5.3	Intrinsic donors obtained by DLTS	102
5.4	Intrinsic acceptors obtained by DLOS	105
5.5	The influence of defects in the net carrier concentration	107
5.6	Conclusions	108
6	Electrical mechanisms for carrier compensation in m-ZnO:N	109
6.1	Introduction	109
6.2	Impact of N in the optical signature	110
6.3	Electrical characterization	111
6.4	Deep level optical spectroscopy measurements	113
6.5	N-related and intrinsic acceptors	116
6.5.1	The intrinsic $E_V + 0.25$ eV trap	116
6.5.2	The N-induced $E_V + 0.48$ eV trap	117
6.5.3	The N-induced $E_V + 0.17$ trap	117
6.5.4	The N-induced $E_V + 0.12$ trap	118
6.6	Conclusions	119
7	Acceptor levels in MgZnO:N	121
7.1	Introduction	121
7.2	Compensation by N incorporation	122
7.3	Deep level optical spectroscopy signatures of N doping	123
7.4	Trap concentrations by lighted CV profiling: the MIS effect	125
7.4.1	The N-related $E_V + 0.47$ eV level	126
7.4.2	The N-related $E_V + 0.35$ eV level	127
7.4.3	The shallow $E_V + 0.16$ eV level	127
7.5	The effect of N implantation on MgZnO	128
7.5.1	Available samples	128
7.5.2	Basic electrical characterization	128
7.5.3	Characterization of implanted samples by DLOS	129
7.6	Conclusions	130
8	Deep level analysis of ZnO heterostructures	133
8.1	Introduction: 2DEG	133
8.2	Deep level optical spectroscopy of heterostructures	134
8.3	DLTS levels measured in heterostructures	137
8.4	Conclusions: Valuable tips for measuring heterostructures	138
IV	Conclusions and future work	141
9	Conclusions and future work	143
9.1	Conclusions	143

CONTENTS

9.1.1	Undoped ZnO layers	143
9.1.2	The effect of N-doping	145
9.1.3	Deep level spectroscopies of MIS structures	148
9.1.4	Equipment improvements and development	149
9.2	Future work	150
9.2.1	Ga-doping in ZnO	150
9.2.2	Residual carrier concentration: undoped samples	150
9.2.3	Depth-resolved measurements: constant capacitance	150
9.2.4	ZnO/MgZnO heterostructures	151
9.2.5	Setup improvements	151
Appendices		153
A ZnO deep levels tables		155
B List of publications and conference participations		169
Bibliography		173

Part I

Introduction and theory

Preface

Document structure

The aim of this PhD thesis is the advancement in the understanding of the p-type doping and defect processes happening in ZnO and ZnMgO materials. A big effort has been placed on improving the characterization techniques, both from the purely technical point of view and from the theoretical understanding of some of the difficulties observed. For tackling all these points, the present document follows the structure presented in the next paragraphs. The main structure is composed of four parts, each containing different chapters.

The **first part** focuses on the theoretical introduction to the materials and devices being used, in order to create a canvas with which the experimental results can be better understood. Chapter 1 describes the material, focusing on the alloying and especially doping perspectives, the Schottky and MIS devices, and the defect states in semiconductors. Then, chapter 2 tackles the practical issues, beginning with device fabrication and basic characterization (current-voltage, capacitance-voltage and photoluminescence). Next, the deep level spectroscopy techniques are presented, which are the core of this thesis, evolving from the theory described in the previous chapter.

The **second part** is dedicated to the developments in the experimental techniques performed during the thesis. The most important result, albeit being the last chronologically, is the adaptation of the deep level spectroscopy techniques to metal-insulator-semiconductor devices (chapter 3). This study arises from the experience obtained in the results presented in part III, and includes a theoretical discussion of the validity of the techniques on the mentioned devices. Chapter 4 describes the improvements performed on the experimental setups, concerning the increased sensitivity, timing characteristics and frequency-dependent measurement features added to the previously existing setups. The experience gained during the research visit to the group led by Prof. Steve Ringel at the Ohio State University (USA) offered an invaluable inspiration towards these advancements.

The **third part** describes the experimental results obtained, most of them having been published in journals. First, chapter 5 shows the results obtained in non-intentionally-doped material grown homoepitaxially by MBE in non-polar and semipolar ZnO. This material was grown by the group led by Dr. Jean-Michel Chauveau at the CHREA-CNRS in France. The intrinsic defect signatures were measured by DLTS/DLOS in these samples, obtaining several levels close both to the conduction and valence bands.

Then, chapter 6 describes the impact of doping with N on m-plane material, grown similarly to the samples from the previous chapter. The defects responsible for the compensation of the material were analyzed, correlating them with the photoluminescence spectra. Analogously, chapter 7 analyzes the deep levels close to the valence band in ZnMgO material grown by MOCVD in Japan by the group of Prof. Jiro Temmyo at

Shizuoka University, also doped with N. The devices processed on this material showed an MIS behavior, thus being necessary the creation of a model to obtain the concentrations from the lighted capacitance-voltage profiles. Several defects responsible for the material compensation were obtained and correlated with the N exposure of the samples during growth. In the same chapter (chapter 7), a description of similar material, implanted with N by Dr. Andrés Redondo at *Instituto de Física Nuclear* at Lisbon, Portugal, instead of doped during growth is shown, which showed no clear indication of the levels observed in the N-grown material. Nevertheless, it is included as an indication of the difficulties posed by the doping in this material. Finally, a study of ZnO/ZnMgO heterostructures as a first step to demonstrate HEMT devices is presented in chapter 8, although a 2-DEG was not observed. However, this analysis was valuable as a first step to understanding trap analysis in these heterostructures.

Finally, **part IV** summarizes the conclusions obtained during this thesis and proposes some future work. An appendix (A) summarizes all the defect signatures obtained during this thesis, and then a table composed from the bibliographical references is shown, with indication of all the electrically active and relevant trap signatures previously found by other groups.

As an additional note on this document, references are organized alphabetically, therefore making the numbering not appear inside the text in their citing order.

Acknowledgments

¿Por dónde empezar? La verdad es que cuesta mucho agradecer el haber llegado hasta este punto, pero sería difícil no empezar por mis padres, que siempre me inculcaron ese amor por la sabiduría y el conocimiento, con un libro acompañándome desde que casi tengo uso de razón. Llegar al punto de discutir investigaciones con tus padres ayuda mucho en este camino difícil que es encontrar algo que se desconoce. Y qué hubiera sido aprender electrónica, cacharrear, programar, sin un clarinete de fondo, ¿verdad, Fede?

Por supuesto, a Adrián tengo que agradecerle el haberme aguantado, primero como alumno en aquella asignatura en que tanto di por saco, llegando a ofrecerme realizar un proyecto que dos años después se convirtió en el germen de esta tesis. Pero no hubiera llegado aquí sin todos los demás profesores que me han acompañado y aguantado durante estos años, especialmente a los de la Universidad de Extremadura, que siempre me apoyaron y ayudaron a avanzar (bueno, siempre no, pero esa es otra historia). Sobre todo a Pilar Suárez, que nos animó a un grupo de lunáticos a participar en aquel club de debate que tanto me ha ayudado después con los congresos, presentaciones, etc.

A toda esa gente de Badajoz (Borja, Juanma, Eu, Rafa...) que siempre me vio por aquí lejos, haciendo mis cosas de cacharritos, pero con quienes tan buenos ratos pasamos (y otros no tan buenos, pero al final nos hemos acabado riendo). Lo mismo puedo decir de la gente aquí en Madrid, que me acogieron al llegar a mitad de carrera (Juan, Itziar, Jaime...), y os seguís preguntando qué narices hago todavía aquí.

Of course, I have to thank a lot the people at Ohio State for having me there, and helping me during my research, despite having so few clear results. Zeng was most helpful, always wanting to help in anything I needed, whether it was scientific or not. Long discussions at the office helped me learn a lot about many things. I must thank Aaron and Steve for letting me use their equipment, which has encouraged me to improve the setups here at the other side of the Atlantic.

During that visit, I also have to thank my american family for showing me what a real Thanksgiving looks like!

About a year later I was received in France, and although the MBE was kind of overused (...) I got the opportunity of learning many things from Jean-Michel and Maxime, for which I thank them thoroughly. Also, for all the great people I met there (Gema!! but also Esther, Michel, Fulvio, Stanislav *coffee* Bodnar, etc). But I need to especially thank Benjamin for finding me a violoncello and a place at the orchestra. The winter in France was a little less tedious playing music. And who could think I could follow a rehearsal... in French?!?!

Por supuesto, no puedo olvidar a toda la gente del ISOM, muchos que me han acompañado durante tantos años que al final he estado rondando por aquí. A algunos los he visto volver (Javi, Miguel), a muchos irse (Gema, Sara, Mariajo, Tomasso...) y cambiar completamente las caras, aunque aún quedamos algunas viejas glorias (¿verdad Antonio, Alberto?). A esos cafés con Cristina, y Rubén, Enrique, Juan. A la gente que está ahora, y me ha visto terminar todo esto (Julen, Alicia, Miguel, Amalia...). Aunque hay caras que siempre te alegran y ayudan, y entre ellos merecen especial atención Fernando, Óscar y Montse, siempre dispuestos aunque sea a tratar el problema, por poca solución que tenga.

Aunque todo esto no podría terminar sin agradecerte a tí, Tamara, haberme aguantado todos estos meses de empujón final, de aguantar el vértigo de ver que todo llegaba y la incertidumbre, pesadez, aburrimiento y hastío con mucho cariño y siempre a mi lado. Por eso estas últimas líneas que escribo quiero que sean para ti.

Chapter 1

Introduction

This chapter introduces the basic theoretical knowledge to create a general canvas in which the next chapters will be framed. First, it introduces the material being used during this thesis, focusing on the doping issues and relevant literature. Next, the physics of the test devices used for the experimental techniques are explained. The remaining sections will describe the dynamic behavior of the defects that can be found in a semiconductor, from the charge and capacitance point of view, since this is the basis for the experimental characterization techniques described in the next chapter.

1.1 Introduction to ZnO

Zinc oxide is a semiconductor material from the II-VI group, stable at room temperature in the wurtzite structure. It has been used for centuries as a white pigment and later, during the early 20th century, the first applications in medicine and cosmetics are found. As a semiconductor, research did not start until several decades later, firstly focusing in its optical properties (photoluminescence and electroluminescence). Since the semiconductor golden age in the mid-1950s, the material has remained as a *promising* material because of its novel properties. In the following decades the piezoelectric properties (1960s), and doping and ion implantation (1970s) were studied. Not until the end of the century did ZnO regain attention because of the advances in nanostructures and the potential as a substitute GaN as the base material for light-emitting devices.

ZnO is a direct bandgap material, with a room temperature bandgap of $E_g = 3.37 \text{ eV}$, and an exciton binding energy of 60 meV [90], much larger than the GaN value of 20-23 meV. Structurally, it forms in the hexagonal (wurtzite) crystalline structure, with lattice constants $a = 3.25 \text{ \AA}$ and $c = 5.207 \text{ \AA}$. This means there is a low crystalline symmetry, which creates piezoelectric effects, with a spontaneous electric field along the c-axis. Chemically, each Zn atom coordinates tetrahedrally to four O atoms. Figure 1.1 shows the crystalline structure for ZnO, in which each atom can be distinguished. In addition, and as it will be shown in a later section, most of the intrinsic defects (vacancies and interstitials) are thermodynamically stable, and are in part responsible for both the intrinsic n-type conductivity (although there is controversy about the involvement of H in this n-type character [23, 48, 79]) and self-compensation shown by the material.

Most of the material grown up to the date, while analyzed optically, has shown a strong defect-band emission (the commonly called green band). Only recently, when high-quality substrates have become available and growth techniques have been improved, this defect band has shown a clear reduction. However, the high n-type con-

Figure 1.1: Crystalline structure for the wurtzite ZnO. The white symbols are O atoms, and the dark ones represent the Zn ones. The two main lattice constants are indicated. Taken from [1]. Plane orientations added by the author.

ductivity still poses a drawback for the development of bipolar devices. Still, promising advances have been obtained, with carrier concentrations as low as $1 \times 10^{14} \text{ cm}^{-3}$ attained in homoepitaxial non-polar material. This opens the path towards high-quality unipolar devices, such as quantum cascade lasers [27], which require a very low defect density.

Because of the lack of reliable p-type doping, despite being for so long a "promising material", ZnO shows applications in the field of ultraviolet (UV) detection. Also, it is being widely used as a transparent conductive layer in solar cells, screens, etc, especially when doped with Al (AZO), Ga (GZO) and Sn (TZO). Another field in which ZnO can pose future applications is for bio-compatible electronics, since it is a non-toxic material, in contrast with GaN and related materials.

1.1.1 Alloying of ZnO

Controlling the bandgap of the material can be interesting both from the optoelectronics point of view (tuning the absorption energy) or in order to create complex heterostructures. Cd and Mg are the choice atoms for bandgap engineering, with the binaries showing bandgaps of $E_{g,\text{CdO}} = 2.3 \text{ eV}$ and $E_{g,\text{MgO}} = 7.8 \text{ eV}$ [4, 30, 54, 106]). However, and differently of what happens with the InGaN system, the binaries crystallize in the cubic structure, being CdO an indirect bandgap semiconductor. Therefore, the bandgaps and lattice constants shown in fig. 1.2 are the result of calculations [54].

Because of the difference in the natural crystallization structure between ZnO and the target binaries, up to certain compositions of the alloyed material, phase separation will occur, limiting the range in which the bandgap can be tuned. The composition at which this phase separation appears depends on the growth method for each material. In the case of Cd, up to the date, a record 70% Cd concentration has been attained [125], whereas for Mg only 56% has been reached [18]. Therefore, the practical range in which the bandgap of the ternary compound can be shifted from 1.8 eV to 4.6 eV, covering the whole visible spectrum and the near ultraviolet.

Electrically, MgZnO has shown some self-compensation, with a lower residual carrier concentration than ZnO grown by the same technique under similar conditions [17, 45].

Figure 1.2: Bandgaps for the different alloys, compared with the InGaIn system. CdO and MgO are shown both in their wurtzite structure (w) or cubic structure (c). MgO(w), CdO(w) and ZnO (c) are introduced from theoretical calculations. Composed from references [30, 54, 106, 107].

This, combined with the asymmetric offset in both bands¹ makes the calculation of complex heterostructures extremely complicated, being this a field with active research. Contrarily, ZnCdO shows a larger residual carrier concentration, with samples having large Cd contents being electrically degenerate. As it will be explained later on this chapter, a good understanding of the intrinsic defects and doping processes is necessary to advance the material towards practical devices and commercial applications.

1.2 Defect states in semiconductors - deep levels

Before talking about doping and the defects observed in ZnO, a general introduction must be placed. It must be remembered that every semiconductor material contains an amount of active impurities, which can be intentional or unintentional. The first group is mostly represented by dopants, that are introduced to change the dominant electrical behavior. They all introduce electronic states inside the forbidden energy gap of the material, as a result of the perturbations induced in the lattice. Ideally, these dopants lie near the main band edges (valence or conduction band), and are thus called shallow-level impurities. From a theoretical point of view, its ionization energy (E_i) can be approximately described by a modified hydrogenic model [68], considering they introduce a single charge without further disturbing the lattice. Since the single charge is introduced in a crystalline system, the effect of the dielectric screening and the reduction of the electron mass shall be included. Therefore, the modified Rydberg series will be:

¹Around 60% on the conduction band (CB) vs. 40% on the valence band (VB).

$$E_i = \frac{m^*}{m_0 \epsilon_r^2} \cdot \frac{13.6}{n^2} eV \quad (1.1)$$

It is important to understand these states, since they constitute the doping levels of the semiconductor, and the minimum observable energy detectable by electrical measurements. Freeze out of the carriers will change the semiconductor behavior to a static insulator, making capacitance transient techniques unavailable.

On the other hand, some of these defects can have ionization energies that lie substantially far from the band edge, originating what are called deep levels. These kind of impurities, which have energies that are strongly concentrated deep inside the band gap, result in charge traps that change the electrical and optical behavior of the material. This type of defects can be intentionally introduced inside the material in order to create recombination centers and/or reduce carrier lifetime to achieve semi-insulating behavior, although they are normally unwanted. The theoretical calculation for these deep levels is extremely complicated, because of their localization effects, relaxation in the lattice, etc. Therefore, the whole bandgap structure must be taken into account, and only powerful techniques such as density functional theory (DFT) or hybrid functional theory (HFT) using large computer simulations have been able to predict the defect behavior.

From their origin, deep levels can be divided into different categories, being the most commonly used nomenclature:

- Foreign impurities: metals, Hydrogen, Nitrogen, etc. If intentionally introduced, they will normally be called dopants.
- Crystallographic point defects: vacancies and interstitials. They can consist of a single atom missing or being added, or there can be complex defects, involving one or more point defects.
- Extended defects: stacking faults and dislocations. They are extended in the lattice, and can act alone as a single level, or they can get "decorated" by other defects, modifying their behavior.

Independently of their origin, the defects can behave differently considering their charge state when ionized:

- Acceptors: states that become negatively charged.
- Donors: states that become positively charged.

However, the aforementioned notation has also been used to differentiate the defects depending on their relative positions with respect to each band. Donors have been said to lie close to the conduction band, and acceptors to the valence band. During the present thesis, when referring to the levels focusing solely on this criteria, they will be named "acceptor-like" and "donor-like", or simply electron or hole traps, in order to avoid confusion. Fig. 1.3 depicts both situations. On the left hand side (fig. 1.3a) the usual situations, where donors lie close to the conduction band and acceptors close to the valence band is shown. The less common situation is shown in fig. 1.3b, and will prove useful in order to explain the dynamics involved in deep level spectroscopy and the results from N-doped ZnO (chapter 6).

Figure 1.3: Energy band diagrams representing the different types of defects, attending to their charge state. (a) Typical configuration with donors and acceptors close to the CB and VB, respectively. (b) Opposite configuration.

1.3 Doping of ZnO

As it has been mentioned in the previous section, ZnO shows an intrinsic n-type behavior, both as a binary material or when alloyed. Despite the many efforts and reports on p-type, no reliable doping procedure has been obtained. Reducing the residual carrier concentration is getting a lot of attention, with record electron concentrations as low as $\sim 1 \times 10^{14} \text{ cm}^{-3}$ having been obtained in non-polar homoepitaxial ZnO grown by MBE [18, 135], which is a necessary step towards p-type conductivity.

It is the objective of this thesis to advance on the knowledge of the intrinsic processes that lead to this situation, although some background will be presented in this section to clarify the state-of-the-art previous to the work presented in this document. In addition, since N has been the dopant used during some of the studies presented in this document, a subsection will be dedicated entirely to the existing knowledge on its effects.

Historically, almost all of the systematic research done on doping in ZnO started in the first years of the present century, concurrent with the availability of high-quality single-crystal substrates, and the development of growth techniques. As is usual in most semiconductor systems, theoretical predictions and experimental results have been published in parallel.

From the theoretical point of view, one of the most productive groups has been that from Chris Van de Walle and Anderson Janotti, from the University of California, Santa Barbara, performing most of the first-principles calculations shown in this section.

Among the existing techniques, the widest used one is Density Functional Theory (DFT²). This technique, developed in the mid 1960s to calculate electron states in many-body systems, by Kohn, Hohenberg and Sham [47, 63], was successfully applied to semiconductor materials with the introduction of corrections to account for complex interactions. Many approximations are used, with Local Density Approximation (LDA) [63] and Generalized Gradient Approximation (GGA) [109, 110].

However, these calculation methods, even with the most accurate approximations, underestimate the bandgap of wide bandgap semiconductors, in order to obtain energy levels that are comparable with experiments. The LDA+U correction [2, 76] takes into account the difference between localized *d* electrons and delocalized electrons, yielding larger values for the material bandgap. Nevertheless, the obtained value is still far from

²In engineering, this acronym can be easily mistaken with Discrete Fourier Transform. If necessary during the text, clarifications will be made, although for this chapter the DFT letters will be used for the Density Functional Theory alone.

Figure 1.4: General diagram for the formation energy and ionization states for a defect depending on the position of the Fermi level position.

the experimental bandgaps. Hence, extrapolation of the energies calculated for the different defect states is needed to correct for the inaccuracies of the method.

Independent of the method used and the needed corrections, these studies yield important information about the particular level under consideration, summarized in fig. 1.4 (whether it is an intrinsic defect, such as vacancies and interstitials, or a dopant impurity):

- **Formation energy.** Represents the energy needed on the system during growth for the level to be formed. This energy is intimately related with the Fermi energy in the material, and the formation energy is thus commonly plotted against this reference (as shown in fig. 1.4). Additionally, for each of the charge states of a defined state, a different plot can be generated. When added all together in a single graph, the crossing points will define the ionization energy.
- **Ionization energies.** These energies represent the Fermi level position at which an energy level will change its charge state. Each defect can have different allowed charge states depending on its nature, and for each one, an ionization energy is defined. Because of its importance, the transition from an uncharged state to its first ionized state is usually called the *activation energy* (E_a) and constitutes an important definition for understanding the deep level spectroscopy techniques which will be defined in chapter 2. In fig. 1.4, the ionization energies for the hypothetical level depicted are shown as dots in the points where the different plots cross one another. As it will be shown later on this section, for the purpose of calculating the energy levels created by a single defect, only the minimum-energy plot (shown in solid black in fig. 1.4) is maintained.

Additionally, a completely new graph can be composed depending on the growth conditions, whether it is cation-rich or anion-rich, showing how each defect is more or less likely to be formed. Therefore, when trying to correlate the calculated energies with the experimental results, the growth conditions must be taken into account.

In the following subsections a particular focus will be placed on the role of the intrinsic defects in ZnO, as well as the doping asymmetry problem which arises in wide bandgap semiconductors, mentioning some of the efforts put in solving the problem.

Finally, a complete review of the literature on N as a dopant has been performed. For the sake of simplicity and clarity, the complete list and tables for the levels and defects observed along the literature have been placed in appendixes at the end of this document (appendix A).

1.3.1 The role of native defects

Let this section begin by defining what is considered a "native" defect. In semiconductor materials, a defect is considered native if it appears without introducing a dopant. They can be point defects or extended defects. Being ZnO a binary material, it can easily be imagined that the most common inhomogeneities that can appear in the lattice are extra atoms or voids, that is: interstitials and vacancies. Throughout this document they will be noted as X_i and V_x , respectively, with x being the atom under discussion. Additionally, extended defects can appear in the lattice, mostly dislocations coming from accumulated stress and stacking faults.

Since certain impurities can get incorporated unintentionally during the growth process, because of the growth technique or from contamination, their effect has been included in this section, albeit them not being native *per se*.

Historically, although work started at the beginning of the 21st century, this section will be heavily based on two reviews that appeared almost at the same time, during 2009. The first one, by McCluskey and Jokela [88] from Washington State University, is dedicated mostly to experimental results. Only two weeks later, Janotti and Van de Walle [53] from University of California, Santa Barbara, published the second work, this time focusing on theoretical calculations of energetic levels, not only by their group, but reviewing the existing literature, and composing fig. 1.5, extremely useful for the deep level characterization researcher in ZnO.

Zinc Vacancy (V_{Zn})

In ZnO, removing a Zn atom from the lattice creates a void with four O dangling bonds, which provide up to six electrons [53], allowing for another two electrons to be trapped. Therefore, zinc vacancies behave as a double acceptor, responsible for some self-compensation in n-type ZnO. The two charge states ($\epsilon(0/-)$ and $\epsilon(-/2-)$) have transition energies of $E_V + 0.18\text{ eV}$ and $E_V + 0.87\text{ eV}$, respectively, according to the first-principle calculations [56]. As it can be observed in fig. 1.5, the formation energy for this defect is higher the lower the Fermi level is. Therefore, while adding acceptors to the material, the "helping" intrinsic V_{Zn} acceptor will be less likely to appear, reducing the effectiveness of the doping process. Additionally, V_{Zn} has been suggested to be involved in a series of complex defects (that ones including two or more "simple" defects, coupled), such as $N_O - V_{Zn}$ [78].

Experimentally, the zinc vacancy has been related to the so-called "green luminescence" observed in PL experiments, with emissions at room temperature around 2.5 eV [85, 88, 89]. Trunk *et al.* suggested that this level is responsible for their DL4 band at $E_V + 0.6\text{ eV}$ [138] and can interact with the other native defects, creating additional PL bands. By means of electrical measurements, only our group has shown the V_{Zn} presence, in MgZnO and ZnO materials grown by different techniques [38, 45, 65, 66]. This will be developed in later chapters in this document.

Figure 1.5: Formation energies depending on the Fermi level and growth conditions: (a) Zn-rich, (b) O-rich. The slopes indicate the charge state for the minimum energy levels. Taken from [53].

Oxygen Vacancy (V_O)

Similarly to the zinc vacancy, a missing O atom leaves four dangling Zn bonds, with three possible charge states (0, 1+, 2+) [52], although the only possible transition is the $\epsilon(0/2+)$ (fig. 1.5). Theoretical calculations differ on the exact value for this defect, due to its situation in the upper half of the bandgap (closer to the conduction band minimum -CMB- than to the valence band maximum -VBM-) and the underestimation of the bandgap yielded by the different calculation methods described earlier on this chapter. However, there is a strong agreement that V_O is a deep donor ($\sim 1 - 2 \text{ eV}$), with a low formation energy, especially in oxygen-rich conditions (fig. 1.5). It can also be observed from the diagram that on n-type material, with the Fermi level laying close to the CBM, the vacancy is in its neutral state, therefore not contributing to the n-type conductivity. Conversely, when reducing the Fermi level energy, by introducing acceptor dopants or reducing the intrinsic n-type character of the material, the V_O can change to its 2+ state, thus compensating the material.

The majority of the experiments identifying oxygen vacancies have been performed by electronic paramagnetic resonance (EMR) and photoluminescence (PL), usually alloying in different environments. The most recent consensus ([52, 88]) is that V_O is responsible for the $g \sim 1.99$ line in the EMR experiments, being illumination needed to observe the charged state, as suggested by the calculations. PL measurements suggest that the emission at 2.53 eV is coming from oxygen vacancies [41], after annealing with Zn vapor. Other measurements indicate transition energies of $\sim 2 \text{ eV}$ [144] and 2.1 eV [26].

Electrically, the V_O has been assigned to both the commonly observed E3 and E4 levels measured by deep level transient spectroscopy (DLTS) [8, 117]. However, due to the charge state and its formation energy, the E3 level is unlikely related to the oxygen vacancy by itself. Recently, Chicot *et al.* [20, 21] suggested that the E3 level might be related to a dual vacancy $V_O - V_{Zn}$.

Zinc Interstitial (Zn_i)

Zinc interstitials have been calculated to be very shallow donors, with charge states above the CBM [52]. It has a high formation energy in n-type material (fig. 1.5), which combined with the low migration barrier [56], makes this defect unlikely to be present in a stable form in material kept at room temperature. However, they can be combined with impurities to create complex defects, which will become stabler and contribute towards the material conductivity.

Oxygen Interstitial (O_i), Zinc antisites (Zn_O) and oxygen antisites (O_{Zn})

These three defects are grouped together since their formation energies (fig 1.5) make them unlikely to appear in as-grown material. The Zn antisite (Zn_O) is supposed to be a shallow donor, although it is only created under non-equilibrium conditions. Zn_O^{2+} has been formed by high-energy electron irradiation, enhancing the n-type conductivity [80]. Oxygen interstitials are electrically inactive, with their donor transition energies occurring below the VBM [56]. Lastly, the oxygen antisite (O_{Zn}) is an acceptor defect, but because of its very large formation energy is not present under equilibrium conditions. However, using implantation and irradiation it could possibly be formed.

Dislocations and stacking faults

Since these constitute extended defects, their theoretical calculation is much more complex than for single point defects. Therefore, the vast majority of the energy levels have been proved experimentally.

As for stacking faults (SF), several reports show a very narrow but intense PL line at 3.31 eV according to Schirra *et al.* [121] or 3.324 eV by Lin *et al.* [77].

In the study by Schirra *et al.*, they relate this 3.31 eV emission, often observed in material doped with group V elements, to stacking faults by means of temperature-dependent cathodoluminescence (CL). They also observe the LO-phonon replicas at 3.23 and 3.16 eV, which could account for the donor-acceptor-pair (DAP) often observed in similar material. However, stacking faults have not been observed in material showing this emission, so its exact origin is still unclear.

On the other hand, Lin *et al.* put the SF-related emission a bit higher in energy at 3.324 eV, also by CL measurements. Interestingly, they perform spatially-resolved scans, obtaining the 3.31 eV emission from the areas close, but not yet scanned, to the SF, whereas when approaching the defect emission goes up to 3.324 eV. They assign this to a screening effect. Similarly, both emissions have been observed in material with no trace of SFs, leaving this results as controversial.

Foreign impurities

This section will be dedicated to the intentional or unintentional impurities that are commonly observed in ZnO, with the exception of N which will have a whole section for itself, since it is the main impurity having been analyzed during this thesis.

Donor impurities Attending to the difference in the electrons, group-III and group-VII atoms are used as donor dopants in ZnO, as summarized in table 1.1. Many elements are available to be included in ZnO, although their study is complicated, because of the native n-type character of the material. In non-intentionally-doped (nid) ZnO, the

Table 1.1: Principal donor-like dopants in ZnO. Composed after [52, 88]

Impurity	Energy (meV)	Reference(s)
Al	120	[155]
Ga	–	
In	–	
F	80	[155]
H	35	[46]

donor energy has been measured by different methods to be 50 meV [90] and even 60 meV [84]. Table 1.1 summarizes the energy positions for the most common dopants in ZnO.

Among them, Al is widely used for transparent conductive films (known commonly as AZO) since very thin films with large conductivities and transparencies can be achieved. Other Group-III elements which have shown n-type doping are Ga and In, with the former having an activation energy around 53 meV [118]. The ionization energy for F in ZnO was calculated to be around 80 meV, although it has not been as widely used as Al as a dopant.

A special mention must be placed on H, since in most of the growth systems it cannot be completely avoided, and its diffusion is very high, being likely its incorporation after the growth. Therefore, in almost every ZnO sample there is a certain amount of H, which gets easily incorporated in the lattice, contributing to the n-type behavior, introducing shallow donor states. While in most semiconductors H behaves as an *amphoteric* impurity (that is, depending on the Fermi level position it behaves either as a donor or acceptor), in ZnO it is only stable as a shallow donor. First-principles calculations [23, 55] indicate that H can exist in a multitude of sites in the lattice: interstitial, substitutional or forming complexes. Many reports are available among the literature describing the H-related donors in ZnO, although they fail to make clear attributions to their exact origin. Values ranging from 35 meV [46] to 300 meV (blaming H for the E3 level [48]) and even higher (E4 at 570 meV [49]).

Acceptor impurities Similarly to what happens for donors, trying to introduce acceptors in ZnO is done by doping with group-V and group-I elements. Li, Na and K have been calculated to introduce acceptor levels in ZnO, although only a brief compensation was observed during experiments. This issue comes probably from self-compensation induced by the formation of donor states (Li_i and Na_i , probably) during the lowering of the Fermi level [91, 108]. There is controversy about the energetics from the Cu-related defects. Whereas first-principles calculations yield acceptor-like levels on the valence band side (700 meV [153]), electrical measurements put the level close to the conduction band (200 meV [35]). The most recent report by McCluskey *et al.* [89] shows a deeper behavior for the Cu level, at 3.21 eV below the CBM.

Leaving N for its own section, group-V elements P, As and Sb are calculated as deep acceptors [42] and even shallow donors [74], existing controversy about the validity of these reports. Some of them even indicate p-type conductivity [40], without consistent

Table 1.2: Principal acceptor-like dopants in ZnO. Composed after [52, 88]

Impurity	Energy (eV)	Reference(s)
Li	0.8	[89]
Na	1.4	[89]
K	–	[108]
Cu	–	[35, 153]
N	*	*
P	–	–
As	–	–
Sb	–	–

studies being able yet to reproduce these findings [53, 89].

1.3.2 Intrinsic defects observed by DLTS

Since DLTS is one the central techniques used during this thesis, along with DLOS, this section will make an overview of the different levels observed using this spectroscopy method in ZnO by the different groups working on this area. A complete list of the publications found to the date is composed in Appendix A.

Very shallow levels Several reports exist in the literature for levels without a label having been assigned to them. For example, Auret *et al.* [7] report levels at 31 and 64 meV, the latter assigned to the Al_{Zn} impurity. The most extended report is that from Ton-That *et al.* [137] that shows a very shallow donor at only 23 meV from the CBM in as-grown ZnO, measured using charge-DLTS (Q-DLTS). This technique was specifically designed to measure shallow defects. H-doped crystals show a splitting of the level in two at 22 meV and 11 meV [137].

E1 This level, first reported by Auret *et al.* [5], is situated at $E_C-0.12$ eV with a concentration in the order of $10^{16} cm^{-3}$ and a capture cross section of $3 \times 10^{-13} cm^{-2}$ and later observed also both in seeded chemical vapor transport (SCVT) and melt-grown (MG) ZnO samples [8]. Several later reports are available in the literature, giving very similar results [7, 122, 143], and attributing this defect to O-rich growth conditions [95].

E2 This level first appeared in an Arrhenius plot by Auret *et al.* [8], who failed to even mention its existence inside the text. However, from the fig. its parameters can be calculated and obtain an activation energy around 100 meV below the CBM, with a capture cross section $\sigma_n = 4 \times 10^{-18} cm^{-2}$. However, many groups have published levels labeled as E2, with different activation energies (0.18 eV [115] and 0.19 [114]). In annealing experiments, this level has been proved to be related to O-rich conditions, although no clear attribution has been made. Quemener *et al.* have related this level to the iron concentration in hydrothermally grown samples [116]. However, this E2 level

has been also observed in MBE material, where Fe contamination is extremely low. Later on this document it will be shown that it is even the dominant peak in DLTS spectra for high-purity homoepitaxial ZnO samples.

E3 This level, first reported in the 1980s by Simpson *et al.* [127] is the most commonly observed defect in ZnO, regardless of the growth technique. With an energy around 300 meV below the CBM, it has been reported that indeed two levels very close in energy can lead to the observed peak (Auret *et al.* report energies of 300 meV and 370 meV [7]). This level has been observed largely among the existing literature, with very similar energy values [29, 115, 140–142].

Ion implantation studies did not show an effect on this level [141] indicating a high stability of the defect creating the peak. Some studies have tackled uniquely this level [7, 21, 48], although reaching different conclusions as for the origin of the E3 peak. In the study by Chicot *et al.* [21], they recall the first-principles calculations, and by combining their own measurements with the literature reports, discard the level to come from one of the point defects, which were initially suggested. Either an impurity is involved, or the E3 level arises from a dual defect (even involving an impurity). Dong *et al.* [25] consider the $V_O - V_{Zn}$ as a suitable candidate. More recently, Hupfer *et al.* [48] showed a possible involvement of H on the origin of this defect, probably in combination with some of the native centers (V_O or O_i).

E4 Firstly published in the study from reference [5], this level yields an energy around $E_C - 570$ meV, with a low concentration ($10^{13} - 10^{14} \text{ cm}^{-3}$) but a large capture cross section $2 \times 10^{-12} \text{ cm}^{-2}$. Later in reference [8] it appears again, but similarly to the E2 level, without being mentioned in the text. By digitizing the Arrhenius plot, an activation energy around 520 meV and a capture cross section of $5 \times 10^{-14} \text{ cm}^{-2}$ can be obtained.

Contrarily to E2, this level has shown in annealing experiments to be related to Zn-rich conditions [117], and even H-related [95]. Several reports have shown similar energies and capture cross sections [29, 48, 115, 140], with the most recent study, dedicated entirely to this defect having been performed by Hupfer *et al.* [49]. They analyze the influence of H during the formation and annihilation of this defect, although the attribution they suggest is the oxygen vacancy (V_O).

E5 and deeper levels Several deep levels have been observed deeper in the bandgap, but their origin or dependence with growth methods and impurities is not clear. A level as deep as 1.06 eV below the CBM [142] has been reported after ion implantation. There is no homogeneity on the labeling of these traps, and further work will be needed in order to fully understand the material. However, this is the region of the bandgap where DLOS can become handy, being easier to photo-excite these defects than thermally activate the energy levels.³

Acceptor-like levels obtained by DLTS Schmidt *et al.* [122] observed by optical-DLTS some minority carrier traps in ZnO, with energies close to the VB of 0.3 and 0.4 eV. Muret *et al.* [97] measured a similar level at $E_V + 280 \text{ meV}$ in homoepitaxial MBE material very similar to the one being used in this thesis.

³As it will be explained later on this chapter, carrier emission from energy levels largely depend on temperature. Additionally, measuring at increased temperatures not only degrades the device properties, but increases the Johnson noise levels, which increase linearly with temperature.

Figure 1.6: Relative positions for the Cu, N, and Li levels in various semiconductors, according to the "universal acceptor level". Reproduced from [89].

1.3.3 Towards p-type ZnO: The doping asymmetry & N-doping

As it was mentioned at the beginning of the chapter, p-type in ZnO has remained elusive. A large number of reports on p-type ZnO exist, and even electroluminescence has been observed. However, the real p-type behavior remains an issue, without the ability to reproduce the results and the suspicion that there is more of a compensation effect than real doping.

Previously, when mentioning most of the native point defects, and some of the dopants, a clear issue arose: lowering the Fermi level induces the formation of donor-like defects that compensate the material. Finding a dopant that creates shallow levels on the opposite side of the bandgap is thus complicated, since wide bandgap semiconductors have either a high CBM or a low VBM [155] compared with narrow bandgap semiconductors. Indeed, fig. 1.6 shows this effect for ZnO, where the broadening of the bandgap compared to other semiconductors occurs because of a relatively low VBM.

Because of its similar atomic radius to O, N has been considered the prime candidate for p-type doping, and both compensation and weak p-type behavior have been reported using this dopant. However, first-principles calculations show that substitutional nitrogen (N_O) is indeed a very deep acceptor, with an activation energy around 1.4 eV from the VBM [52, 86]. Experimentally, Tarun *et al.* [136] showed that a PL emission around 1.7 eV can be attributed to N. More recently, McCluskey *et al.* confirmed those results, observing an acceptor state at 1.4 eV above the VBM.

However, many reports exist among the literature indicating shallow acceptor levels related to N, in the range of 130-200 meV, mainly from PL measurements, where an intense donor-acceptor-pair (DAP) emission is observed. Indeed, this DAP has, up to the date, only been observed in N-doped material, at low-temperature PL energies around 3.23 eV. As of 2005, D. Look [82] published a review of all the p-type ZnO reports, with the attributions and acceptor energies observed.

Further characterization of this DAP emission [130, 154], yielded an acceptor energy of 165 meV, coupled with a donor activation energy of 52-54 meV. Despite this donor to be clearly present in the PL-observed DAP, the report by Muret *et al.* [97] that

characterized N-doped m-ZnO grown by MBE did not observe such a shallow donor level by electrical measurements. As for the defect creating that acceptor level, the simple N_O origin can be ruled out. Therefore, many groups tried to perform calculations on the possible sources for the observed defect. Nickel and Gluba [102] suggested that molecular N_2 , when breaking a Zn-O bond, can create an acceptor level at $E_V + 170\text{ meV}$. However, this level alone does not lead to persistent p-type conductivity, usually compensating the layers. Even in very low residual concentration samples (with residual carrier concentration in the reference sample as low as $1 \times 10^{14}\text{ cm}^{-3}$), Tainoff *et al.* could only obtain fully-depleted semi-insulating layers.

The reports for N-induced DAP emissions continue [33, 34, 70–72, 98, 129, 131, 135, 148], with energies as low as 130 meV [119]. They attributed that acceptor level to a complex defect involving N and H, $N_O - V_{Zn} - H^+$. This correlates well with the calculations from Liu *et al.* [78], who propose the $N_O - V_{Zn}$ complex defect as an acceptor level with activation energy 160 meV above the VBM. However, more recently, Bang *et al.* [11] recalculated this defect to be a deep acceptor, by removing the assumption that the defect might be non-magnetic, and increasing the supercell size from 72 to 300 atoms.

Despite the identification of shallow acceptors in N-doped ZnO, and the many attributions been made, the reality is that no reproducible p-type doping has been obtained for ZnO. In addition to the doping asymmetry described in previous sections, many issues arise when trying to dope, as well as in some of the experiments found in the literature. Careful treatment of the samples is needed, as proved by Claflin *et al.* [22], who observed persistent n-type photoconductivity in weak p-type ZnO, measured by Hall effect. This persistent photo-effects have also been observed by other groups [66, 112], with decay times after over-bandgap illumination several days long.

In order to achieve p-type doping, many approaches have been proposed, after the most straightforward options have shown their lack of success. The first and most obvious one will be reducing the number of native donor concentration, reducing impurities and intrinsic defects, although this approach has not yet yielded p-type material. Pushing the VBM up in energy, so that the acceptor levels come closer to the band, or even get shifted towards effective-mass dopants (that is, their energy level lies below the VBM), could enhance the doping efficiency [87]. Co-doping, where two or more dopants are introduced at the same time, can also help to avoid the self-passivation of the introduced acceptors.

1.4 Schottky barrier diodes

A Schottky barrier, also known as metal-semiconductor junction, is formed by the contact between a metal and a semiconductor material. Later in the 19th century, the first observation of a rectifying behavior was performed, being the model that describes the physics of the device improved during the first half of the 20th century.

In the ideal case, where the interface between metal and semiconductor is perfect, and there are no surface states, both materials will form a single system, in which the Fermi level on both sides will be aligned, as shown in Fig 1.7. When the materials are independent, their alignment is relative to the vacuum level, being the work function in the metal defined as the difference between its Fermi level and the vacuum level, denoted as $q\phi_m$. For the semiconductor, its electron affinity, written as $q\chi_s$, is defined as the difference between the bottom of the conduction band (E_C) and the vacuum level. The

Figure 1.7: Band diagrams showing the formation of the Schottky barrier for an n-type semiconductor material. (a) Both materials separated. (b) Schottky barrier in equilibrium.

difference between E_C and the Fermi level is shown as $q\phi_b$.

When the materials are put into contact, a negative charge is built up in the metal surface, creating an equal and opposite positive charge in the semiconductor, generating an electric field. The region of the semiconductor in which this field drops is called the depletion region or space-charge region. Both terms will be used indistinctly during this thesis. The barrier created between both materials will therefore have a height given by:

$$q\phi_b = q(\phi_m - \chi_s) \quad (1.2)$$

Electrons with an energy high enough will be able to cross the barrier, contributing towards the conductivity of the device. This barrier height, as well as other parameters that define the operation of the Schottky device, can be obtained from experimental measurements, as will be discussed in chapter 2.

1.4.1 Depletion region in a Schottky barrier

As it has been mentioned in the previous paragraphs, by creating a metal-semiconductor device, a depletion layer is created in the semiconductor side because of the band bending induced by the alignment of the Fermi levels. The width of this region is given by [12, 132]:

$$W_d = \sqrt{\frac{2\varepsilon}{qN} (\phi_{bi} + V_a)} \quad (1.3)$$

Where ε is the dielectric constant of the depleted material, ϕ_{bi} is the built-in bias voltage of the junction, and V_a is the externally applied voltage, q is the charge of the electron, and N is the density of ionized doping centers. In a later section, it will be shown how the variation with time (transient behavior) of this parameter affects the depletion region.

As it can be observed in Eq. 1.3, the depletion width is proportional not only to the intrinsic characteristics of the material (workfunction, electron affinity, dielectric constant or carrier concentration), but also on the external applied voltage. This fact is the base for all the space-charge based techniques described in the following chapter. Figure 1.8 shows the different band diagrams for a Schottky diode when a bias is applied.

Figure 1.8: Band diagrams for a Schottky barrier on n-type material. (a) Junction under equilibrium. (b) Forward bias. (c) Reverse bias.

As it can be observed, the bands will flatten with forward bias (fig. 1.8a), shrinking the depletion region towards the surface. On the other hand, when applying reverse bias (fig. 1.8b), the depletion region is increased, by enhancing the band bending. It is important to mention that for p-type material, the behavior will be similar, with the bending occurring in the opposite direction.

1.4.2 Junction capacitance

As it has been previously mentioned, a reverse biased junction creates a space charge region between materials. Assuming the carrier concentration along the depletion region is constant, the semiconductor charge will be given by:

$$Q_s = q \int_{x=0}^{W_d} N dx \quad (1.4)$$

Which for $N = N_D$ under steady state conditions, and including eq. 1.3 yields:

$$Q_s = qN_D W_D = \sqrt{2q\epsilon_s N_D (\phi_{bi} - V_a)} \quad (1.5)$$

Therefore, it is straightforward that the capacitance of a reverse-biased Schottky diode is given by:

$$C_d = -\frac{dQ_s}{dV} = qN_D \frac{dW_D}{dV} \quad (1.6)$$

In this situation, the depleted junction can be imagined as a parallel plates capacitor, for which the capacitance is known to be:

$$C = \frac{\epsilon A}{W} \quad (1.7)$$

Again, ϵ is the dielectric constant of the material in which the depletion region lies, where A is the diode area, and W the distance between plates. In this case, W is given by equation 1.3.

Combining equations 1.3 and 1.7, the junction capacitance can be described as:

Figure 1.9: Capacitance as a function of reverse bias in an n-type Schottky diode.

$$C_d = \varepsilon A \sqrt{\frac{qN}{2\varepsilon (V_{bi} + V_a)}} \quad (1.8)$$

Although this expression is fairly simple, it is powerful enough to allow for the characterization of many different parameters in a Schottky diode, and will be recalled several times during this thesis. Figure 1.9 shows a plot of the capacitance given by eq. 1.8 for a general n-type material. The measurement and analysis of this kind of plots will be thoroughly used in the second chapter of this thesis.

1.5 Metal-insulator-semiconductor diodes

Metal-insulator-semiconductor (MIS) devices have been widely used for the study of semiconductor surface properties, and are also the basic component of most of the field-effect transistors used for modern digital electronics (mostly based on Si/SiO₂ MOS technology). However, as shown in some studies [15, 61, 66, 100], an unintentional insulating layer can appear between the metal and the semiconductor in a target Schottky diode.

In the ideal situation, where no charge is trapped inside the insulator nor in the interfaces, no bias is applied, and there does not exist transport through the insulator, the band diagram of the device will be as shown in fig. 1.10a. There, E_i has been defined as the mid-bandgap energy, χ_i and χ_s are the electron affinities of the insulator and the semiconductor, and ϕ_B & ϕ_f are the Fermi level positions relative to the midgap and conduction band, respectively, which for fig. 1.10 are assumed equal. It must be noted that for the following discussion to be accurate, the insulator is assumed not to allow the flow of current through the device. Therefore, although in real devices tunneling and thermoionic transport processes exist, this section considers those effects to be negligible.

However, Φ_b and Ψ_s are different, with this difference being given by:

Figure 1.10: Band diagram for an MIS formed on n-type semiconductor in the ideal condition. (a) Without bias applied. (b) Reverse bias applied. Composed assuming $\Phi_b = \Psi_s$

$$\phi_{ms} = \phi_m - \left(\chi_s + \frac{E_g}{2q} - \phi_B \right) \quad (1.9)$$

Where

$$\phi_B = \frac{kT}{q} \ln \left(\frac{N_D}{n_i} \right) \quad (1.10)$$

If ϕ_{ms} is zero without an applied bias (that is, the workfunctions for both metal and semiconductor are equal), the bands will be flat at zero bias, although this is normally not the case in real devices. Fig. 1.10b, shows the situation in which a bias ($V < 0$) is applied to the device. In it, the surface potential is marked as ψ_s , and from its relative magnitude and sign with respect to ϕ_f , several regimes can be distinguished:

- $\psi_s > 0$: Accumulation
- $\psi_s = 0$: Flat-band
- $\phi_f < \psi_s < 0$: Depletion
- $2\phi_f < \psi_s < \phi_f$: Weak inversion
- $\psi_s = 2\phi_f$: Threshold condition
- $\psi_s < 2\phi_f$: Strong inversion

The energy band diagrams for each case are shown in fig. 1.11. The first regime, which happens for positive applied voltages, is the *accumulation* regime. Because of the positive potential in the metal, a similar but opposite in sign charge will appear at the surface of the semiconductor, creating what is called the accumulation layer. This effect makes the device behave as a parallel plates capacitor, with a capacitance equal to the insulator capacitor (C_{ins}), which can be calculated as

$$C_{ins} = \frac{\epsilon_{ins} A}{d}. \quad (1.11)$$

Figure 1.11: Band diagrams for an MIS device on n-type material under the different operation regimes. (a) Accumulation, (b) flat band, (c) depletion, (d) weak inversion, (e) threshold and (f) strong inversion.

As the bias is reduced from 0 V (ideally, flat band condition - fig. 1.11b), the bands start bending downwards, first appearing a depletion region, similar to that already described for the Schottky diode (fig. 1.11c). However, when a certain voltage is reached that makes the midgap level cross the Fermi level (or, more technically, $2\phi_f < \psi_s < \phi_f$ - fig. 1.11d), some holes are allowed to be trapped in the surface, creating a layer which is in fact, inverted in type compared with the semiconductor material. This is called the *inversion* regime, which starts as a weak inversion, when the minority carrier layer is not fully formed.

Once a voltage is reached that makes $\psi_s = 2\phi_f$, the inversion layer will be fully formed. This is called the *threshold* condition, and the voltage at which it occurs, the *threshold Voltage* (V_t). In fig. 1.11e it can be observed how in the threshold condition, the amount of midgap level which lies above the Fermi level in the surface equals ϕ_f . This is a graphical and easy way of finding the threshold condition, for example, in simulation software that does not directly calculate V_t . Analytically, the threshold condition can be written as

$$\psi_s = 2\phi_B = 2\frac{kT}{q} \ln \frac{N_D}{n_i}. \quad (1.12)$$

The inversion condition will indeed pose a limit to the maximum width the depletion region can reach, before becoming completely screened by the inversion layer. This maximum depth will be reached at the threshold condition, and will have a value given by

$$W_{d,max} = \sqrt{\frac{2\epsilon_s\phi_{s,inv.}}{qN_D}} = \sqrt{\frac{2\epsilon_s2\phi_B}{qN_D}} \quad (1.13)$$

which can be rewritten as a function only of doping and intrinsic semiconductor parameters:

$$W_{d,max} = 2\sqrt{\frac{\epsilon_s kT \ln(N_D/n_i)}{q^2 N_D}}. \quad (1.14)$$

The charge in the depletion region can be calculated similarly as for the Schottky diode case, as

$$Q_d = qN_D W_{d,max}. \quad (1.15)$$

Fig. 1.12a shows the charge densities in the metal (ϕ_m), the inversion layer (ϕ_{inv}) and the depletion layer (ϕ_d). The total charge in the semiconductor will therefore be the sum of the inversion and the depletion charges, and will be equal in magnitude and opposite in sign to the charge in the metal:

$$\phi_s = -\phi_m = \phi_{inv} + \phi_d \quad (1.16)$$

In fig. 1.12b it can be observed how the total applied voltage (V_a) drops between the insulator (V_i) and the semiconductor (ψ_s).

$$V_a = V_i + \psi_s \quad (1.17)$$

In the ideal case, this voltage drop can be written as

Figure 1.12: Charge density (a) and Electrostatic potential (b) in an MIS device under the inversion regime.

$$V_i = \frac{-Q_s d}{\epsilon_{ins}} = \frac{-Q_s}{C_{ins}} \quad (1.18)$$

Where $Q_s \approx Q_d$, as given by eq. 1.15 and C_{ins} can be obtained from eq. 1.11. Therefore, from fig. 1.12b and the previous expressions, the threshold voltage for the ideal case is

$$V_T = \psi_{s,inv} + V_{i,inv} = 2\phi_F - \frac{Q_d}{C_{ins}} \quad (1.19)$$

All the expressions shown so far are valid only for ideal cases, in which there does not exist trapped charge in the insulator nor is there a difference in workfunction between the metal and the semiconductor ($\phi_{ms} = 0$). However, this is normally not the case. As shown thoroughly in the literature ([132]), the final expression will have to include both terms, as shown in the more complete expression:

$$V_T = \phi_{ms} - \frac{Q_i}{C_i} - \frac{Q_d}{C_i} + 2\phi_F \quad (1.20)$$

1.5.1 Capacitance in MIS devices

Similarly to the case of the Schottky diode described in the previous section, the MIS device will show a certain capacitance, which will be dependent on the applied voltage and on the operation regime that voltage creates. Also, frequency has an impact on the capacitance the device shows under the inversion regime.

The total capacitance of the device will be the series combination of the insulator and the semiconductor capacitances (C_{ins} and C_s , respectively):

$$C_{total} = \frac{C_{ins} \cdot C_s}{C_{ins} + C_s} \quad (1.21)$$

Where C_{ins} is given by eq. 1.11. However, since the charge distribution depends on the operation regime, the semiconductor capacitance will change accordingly. Under accumulation, as it was already shown in the previous section, a thin layer of majority carriers appears on the surface, without a depletion layer. Therefore, the total charge in the semiconductor will be that of the accumulation layer, which will resemble a perfect

Figure 1.13: Capacitance-Voltage profile for an MIS on n-type material, with indication of the operation regimes and the relevant parameters. The operation at low, medium and high frequencies is shown for the inversion regime, as well as the deep depletion effect.

Figure 1.14: Transversal representation of the charge distribution in an MIS device (top) and its charge density graph (bottom) for the accumulation (left) and the depletion (right) regimes.

parallel plates capacitor, with a capacitance equal to that one coming from the insulator layer (C_{ins}), as shown in fig. 1.14.

In the depletion region, the space charge width is given by the same expression as for the Schottky case (eq. 1.3), only taking into account that the voltage now is not equal to the applied voltage (1.17). Therefore, combining eqs. 1.3 and 1.17:

$$W_d = \sqrt{\frac{2\epsilon}{qN}} (V_{bi} + V_d) = \sqrt{\frac{2\epsilon}{qN}} (V_{bi} + V_a - V_i) \quad (1.22)$$

Which yields to a depletion capacitance of

$$C_d = A \sqrt{\frac{q\epsilon N}{2(V_{bi} + V_d)}} \quad (1.23)$$

Thus, as long as the device is biased in the depletion region, the total capacitance will be simply the series combination of C_{ins} and C_d , up to the maximum depletion

1.5. METAL-INSULATOR-SEMICONDUCTOR DIODES

Figure 1.15: Transversal representation of the charge distribution in an MIS device (top) and its charge density graph (bottom) for the inversion regime at low frequency (left) and high frequency (right).

(given by eq 1.14), which yields to a minimum achievable capacitance:

$$C_{d,min} = A \sqrt{\frac{q^2 \epsilon N_D}{4kT \ln(N_D/n_i)}} \quad (1.24)$$

Under the inversion regime, there is a dependence of capacitance with the probing frequency and sweep rate, as depicted in fig. 1.15. The difference comes from the fact that an n-type material is a poor source of holes (analogously, p-type material is a poor source of electrons), and the thermal generation for minority carriers is very slow. If the AC frequency is slow enough, Q_{inv} can follow the changes in voltage, and the surface inversion layer will act as one of the charged layers in a parallel plates capacitor. However, when the AC frequency is further increased, Q_{inv} cannot follow the changes in bias, and the incremental charge will be placed at the end of the depletion region (fig. 1.15). Therefore, the total capacitance will be a combination of the depletion and the inversion capacitances, being the inversion capacitance equal to the insulator capacitor. Since the depletion width is already at its maximum value, the inversion capacitance at high frequencies will be fixed at C_{min} , as shown by the low-frequency C-V profile (1.13). It is important to mention that for intermediate frequencies, the inversion capacitance will be a combination of the low-frequency and the high frequency values, which will prove useful for the study of N-related acceptors in MgZnO shown in chapter 7.

There is one situation, unique to MIS structures, called *deep depletion*. It occurs when the sweep rate from depletion to inversion is performed too fast for any of the minority carriers generated when crossing the threshold voltage is allowed to move to the surface and create the inversion layer. Under this circumstance, all the generated charge is placed at the end of the depletion region, pushing it deeper than $W_{d,max}$, obtaining capacitances lower than $C_{d,min}$, as shown in fig. 1.13. For deep level spectroscopy techniques, it is important to take this situation into account, since during the bias pulses the threshold voltage⁴ can be crossed. As it will be further explained in chapter

⁴Recalling eq. 1.20, it can easily be observed that V_T is dependent on parameters that can change

Figure 1.16: Equivalent circuit for an MIS device including the general elements for both the inversion and depletion regimes.

3, correctly biasing an MIS device is crucial for the measurement to be feasible.

As a summary, an equivalent circuit can be composed, as shown in fig. 1.16, including all the aforementioned capacitors plus the semiconductor equivalent resistance. Although this parameter does not play a special role under the steady-state conditions described in this section, it will be useful for the dynamic operation which will be the basis of chapter 3. Also, the capacitance of both the depletion region and the inversion layer are included. Under strong inversion, however, the capacitor resulting from the addition of the inversion and the depletion contributions is extremely high, in comparison with C_{ins} that the total capacitance will tend towards the latter.

1.6 Capture-emission kinetics

For the concerns of the present study, deep levels do not behave statically, but they show a dynamic operation, which is what is commonly referred as capture-emission kinetics. In order to understanding this process, a brief explanation will be presented, continuing with the equations that govern the dynamic operation of these charge traps.

1.6.1 Equilibrium carrier statistics

In the absence of thermal energy, the Fermi distribution, given by

$$f(E) = \frac{1}{1 + e^{(E-E_f)/kT}} \quad (1.25)$$

will define a square distribution. That is, no electrons are allowed above the Fermi level (E_f). For the case of an n-type semiconductor, with a donor level laying very close to the conduction band, for very low temperatures, there will not be enough thermal energy for the level to become ionized, and there will be no electrons available in the conduction band ($n \approx 0$). Therefore, the semiconductor will behave nearly as a dielectric, or will be *Frozen out*.

As the temperature is increased, more and more electrons will gain enough energy to be excited onto the conduction band, until a certain temperature is reached in which $n \approx N_D^+$, or more plainly, the dominant donor level will be fully ionized. This regime is called the *extrinsic region*, and is maintained up to a certain temperature in which eq.

with temperature, carrier concentration, etc. Therefore, during a spectroscopy scan, its value will not remain constant.

Figure 1.17: Capture-emission for deep level impurities. e_x and c_x represent the emission and capture rates, respectively, whereas n and p reference electrons or holes.

1.25 allows for the electrons in the valence band to gain energy to be moved directly to the conduction band, reaching the *intrinsic region*. An extended description of the carrier statistics can be found in many textbooks [111, 132].

1.6.2 Dynamics of deep states in semiconductors

The physics behind the generation and recombination processes in semiconductor was first proposed independently by Shockley and Read on the one hand [126], and Hall on the other one [39], thus being commonly called as the Shockley-Read-Hall theory. However, this chapter will be based on the later description by Pierret [111] and Kaplar [59].

Figure 1.17 depicts the four basic transitions that can occur between a defect state and the semiconductor bandstructure, basically, capturing and emission of any carrier. However, depending on the nature of the level and its distance from the bands, each process may occur at a different rate. In the following paragraphs these differences will be analyzed. It is important to mention that the energy needed for any of these process can be thermal or optical, and can involve excitons.

Figure 1.17 shows a deep level with an energy E_T that lays at the middle of the band-gap. In this theoretical case, the trap will be assumed to be uniformly distributed throughout the material, with a concentration of N_T impurities/cm³. The semiconductor itself has n electrons/cm³ and p holes/cm³ due to shallow-level dopants, being:

$$N_T = n_T + p_T \quad (1.26)$$

As it has been already pointed out, two processes are present in the dynamic behavior of traps:

- Capture (c_x). This process happens when either an electron is captured from the conduction band to the trap, or a hole from the valence band is trapped inside a defect.
- Emission (e_x). This process is the opposite to capture, and it represents the emission of a previously captured electron towards the conduction band, or a hole back to the valence band.

The rate at which these processes occur will be proportional to the band occupancy (n or p) and the density of occupied or empty traps (n_T or p_T , respectively). Let us first consider an electron capture, for which we can write

$$\frac{dn_T}{dt} = c_n np_T \quad (1.27)$$

where c_n is defined as the *electron capture coefficient*, and will be expressed normally in s^{-1} . It is straightforward to think of the electron emission, which is only proportional to the density of filled traps (assuming that the trapped electron will always find an empty level in any of the bands).

$$\frac{dn_T}{dt} = -e_n n_T \quad (1.28)$$

where e_n is called the *electron emission rate* with units of s^{-1} . Analogously, for the hole capture and emission processes, it can be written:

$$\frac{dn_T}{dt} = -c_p p n_T \quad (1.29)$$

$$\frac{dn_T}{dt} = e_p p_T \quad (1.30)$$

Therefore, the net change in the trap occupancy will be obtained as

$$\frac{dn_T}{dt} = c_n np_T - e_n n_T - c_p p n_T + e_p p_T \quad (1.31)$$

However, there is a dependency between the capture and emission coefficients. In order to deduce this dependency, let us write that under steady-state conditions, the net rate of change between the emission and capture processes must be zero. For an electron trap

$$c_n np_T - e_n n_T = 0 \quad (1.32)$$

which yields an emission rate:

$$e_n = c_n n \frac{p_T}{n_T} = c_n n_i e^{\left(\frac{E_i - E_T}{kT}\right)} = c_n N_C e^{\left(\frac{E_T - E_C}{kT}\right)} \quad (1.33)$$

It can be easily observed from eq. 1.33 that the electron emission rate is dependent principally on the temperature and trap position.

Different combinations of both processes can occur, and lead to the description of two major events:

- Recombination, when two capture processes from opposite bands happen, "moving" a carrier from the conduction band to the valence band, or vice versa.
- Trapping. In this case, the capture process is followed by an emission back to the band from which the carrier was originally trapped.

Which mechanism dominates the behavior of a deep level depends on various parameters, such as the Fermi level energy, temperature and the effective capture cross section of the impurity. Normally, levels that lie near the middle of the band gap behave as recombination centers, whereas those with energies near the band edges act as traps.

During the following sections of this document, impurities are assumed to behave as traps. Also, for those levels with energies in the upper half of the bandgap, the electron emission rate will generally be much larger than the hole emission rate, and the opposite applies for those centers with energies in the lower half of the bandgap.

Figure 1.18: Dynamic operation for a deep level close to the conduction band (E_C) during a fill pulse (a) and immediately after returning to the reverse bias condition (b).

1.7 Space charge transients

In the previous section the principal mechanisms involved in trap behavior have been mentioned. Attention will be focused on these events when they occur in the depletion region of a device, as it is the material region explored with deep level spectroscopy measurements. Under these conditions, capture rates can be assumed to be zero much lower than the emission rates during the transients following a fill pulse. Similarly, during this filling pulse, capture rates can be assumed to be not only higher than the corresponding emission rate, but also fast enough to allow for the traps to be completely filled in the time the pulse lasts.

Figure 1.18 shows the transient operation for a trap, close to the conduction band (E_C). As it can be observed, when the bias is moved towards values less negative than the steady-state operation, the depletion region shrinks and for a certain volume in the material, the energy level corresponding to the defect (E_T) lays below the Fermi level, thus allowing for electrons to be captured at a rate equal to c_n .

Following this fill pulse, a reverse bias is applied again, as shown in fig. 1.18b. The electrons that were trapped now lay above the Fermi level, and will then be emitted back to the conduction band. This process will occur at the electron emission rate, defined in eq. 1.33, which can be rewritten as [12]:

$$e_n(T) = \sigma_n v_{th} n_i e^{-\frac{\Delta E}{kT}} \quad (1.34)$$

where σ_n is the trap capture cross section, and depends on the nature of the particular defect; v_{th} is the thermal velocity of the electrons and n_i represents the effective density of states in the region where the carriers are emitted, and $\Delta E = E_C - E_T$. Also:

$$v_{th} n_i = \gamma_n T^2 \quad (1.35)$$

The constant γ_n depends on the material electron effective mass (m_n^*) as $3.25 \times 10^{21} \times m_n^* (cm^{-2} s^{-1} K^{-2})$. It is important to note that some authors describe trap operation not from the conduction band, but from the valence band.

For the purpose of transient operation, it is sometimes more useful to rewrite equation 1.34 in the form of a time constant:

$$\tau_n = e_n^{-1} = (\sigma_n \gamma_n T^2)^{-1} e^{\frac{\Delta E}{kT}} \quad (1.36)$$

During the transient immediately following a fill pulse, it can be assumed that the dominant processes are both hole and electron emission. Thus, the rate at which the trap occupancy changes with time is given by

$$\frac{dn_T}{dt} = -e_n n_T + e_p p_T \quad (1.37)$$

As it has been previously described, in most traps only one process is dominant, making it possible to simplify equation 1.37 taking into account only the dominant term. Solving this differential equation gives the time evolution of the carrier concentration in the trap:

$$n_T(t) = n_T(0) e^{-e_n t} = N_T e^{-\frac{t}{\tau_n}} \quad (1.38)$$

If instead of considering thermal emission, photons are shone into the depletion region of a semiconductor material containing defects, their occupancy will change, following a variation of eq. 1.37:

$$\frac{dn_T}{dt} = -\sigma_n^o + \Phi n_T + \sigma_p^o \Phi p_T \quad (1.39)$$

where σ_x^o are the optical cross sections for both electrons and holes, and Φ is the photon flux at the given energy.

1.8 Capacitance transients

From fig. 1.18 it can also be observed that there is a difference in the depletion width between the fill pulse voltage and the reverse biasing conditions, defined as ΔW_d . Eq. 1.8 shows that for a Schottky diode the capacitance depends on the carrier concentration, which was defined as a constant value at the time. Under transient operation, eq. 1.8 can be modified, substituting the steady state carrier concentration with the temperature and time dependent value, which can be assumed to be $N = N_D - n_T(t)$, as donors are fully ionized. Taking that into account, substituting equation 1.38 and operating the resulting equation leads to a description of the capacitance transient behavior in depleted regions:

$$C(t) = C_\infty \left[1 - \frac{N_T}{2N_D} e^{-e_n t} \right] \quad (1.40)$$

Here, e_n is given by equation 1.34, that describes the variation with temperature of the emission rate. C_∞ represents the steady-state capacitance that the junction reaches once the traps are empty. This type of transients are the basis of DLTS, as will be explained in chapter 2.

1.9 Optical processes in semiconductors

Up to this section all the processes described have been related to the capture or emission of carriers because of their thermal energy. However, both capture and emission can be forced by the action of photons with an energy resonant with the levels. Moreover,

Figure 1.19: Optical processes in semiconductors for: (a) Band-to-band transitions; (b) Excitonic transitions; (c) Acceptor-related transitions; (d) Donor-acceptor transitions and (e) Donor-related transitions. These processes work for absorption (left-hand side -abs-) and emission (right-hand side -em.).

these processes can involve the action of phonons and excitons, generating a complex combination of mechanisms for the carriers to be optically transported along the material.

Absorption Absorption is defined as the process in which a photon with sufficient energy donates enough energy to a carrier to be excited from its present position to another available state. Momentum must be conserved, so this process can involve the contribution from a phonon. It can be written as:

$$E_x = h\nu \pm E_p \quad (1.41)$$

being E_x the energy difference between the two allowed states, $h\nu$ the photon energy and E_p the phonon energy.

Emission Similarly to absorption, the transition between a high-energy state and a low-energy level can involve the emission of a photon of a certain energy, equal to the difference between the levels.

Figure 1.19 summarizes the different optical processes that can happen in a semiconductor material. They will be explained in the following paragraphs in this section.

1.9.1 Band-to-band transitions

If a photon is absorbed, with energy enough for an electron on the valence band to be excited up to the conduction band, an electron-hole pair will be generated, which can then contribute to the device conduction (1.19a). If these transitions, in order to conserve momentum, need of the absorption or emission of a phonon, will be called indirect transitions. On the other hand, if they do not involve phonons, they are called direct transitions. Therefore, a semiconductor material in which photons can be absorbed without emission or absorption of phonons, is said to have a direct-bandgap, as is the case of ZnO.

Similarly, if a certain number of free electrons occupy the conduction band, after a certain time (called the radiative lifetime of the electrons), they will be relaxed to the lower valence band energy, emitting a photon with an energy equal to the bandgap. If the occupancy of the conduction band is high, several transitions will be allowed with energies larger than the bandgap, broadening the emission peaks obtained by measurements.

1.9.2 Excitonic transitions

Although the exciton has been mentioned before in this document, it has not yet been defined. An exciton is simply the combination of an electron and a hole held together by coulomb attraction. The electron orbits the hole following a hydrogenic model. The energy needed for this coupling to be dissociated is called the *exciton binding energy*. The recombination of these coupled particles creates a very sharp emission at an energy

$$h\nu = E_g - E_{exc} \quad (1.42)$$

This situation is depicted in fig. 1.19b. Moreover, the excitons can be bound to the impurities found in the lattice, such as acceptors and donors, resulting in a reduced energy level for the combined particles.

1.9.3 Defect-driven transitions

An electron situated in a defect can absorb a photon or a phonon or be emitted, creating a photon, with an energy lower than the bandgap. For defect-to-band transitions, the probability of the transition will be higher than for the defect-to-defect one, because of the physical distance that can exist between the two defects, which can be larger than the mean free path of the carriers.

1.9.4 Optical parameters of ZnO

From the beginning, ZnO has been considered as a good material for optical applications, being a direct-bandgap semiconductor, with a room-temperature gap of 3.37 eV, similar to that from GaN. Its exciton binding energy is larger, with a value of 60 meV. This makes the free exciton stable at room temperature. The phonon energy is also large, of 72 meV, which is useful for the design of infrared inter-subband devices.

Chapter 2

Characterization and processing techniques

2.1 Device fabrication

This first section will devote to the processing of the test devices used during the research, which have been mainly Schottky diodes. The different steps and considerations are thus included in this section.

2.1.1 Material growth

During this thesis, ZnO grown by two main techniques have been used. First, remote-plasma-enhanced metal-organic chemical vapor deposition (RPE-MOCVD) MgZnO samples grown by Prof. J. Temmyo from Shizuoka University in Japan were obtained. The details will be explained in the chapter dedicated to those samples.

A second group, providing the rest of the samples shown in this thesis was grown by Dr. J.M. Chauveau from the *Centre de Recherche sur l'Hetero-Epitaxie et ses Applications* (CRHEA) from the CNRS in France. They were grown by molecular beam epitaxy (MBE), homoepitaxially in non-polar and semipolar substrates.

2.1.2 Device processing

As it was explained during chapter 1, Schottky diodes have been the main test device used for all the capacitance-based characterization techniques. Independently of the substrate, orientation or growth method, the processing steps have been the same, using the recipe developed by Dr. Gema Tabares, which has shown very good results [133,134]. The only modification has been the design and implementation of a new lithography mask that allows for the processing of a denser matrix of diodes, as well as adding contact pads to the semi-transparent Schottky diodes. A schematic of the device, plus a microscope image of a finished diode, can be observed in fig. 2.1. The processing steps are as follows:

Cleaning Since Schottky diodes are planar devices, eliminating any trace of impurities that can reduce the performance is crucial. Samples were rinsed in acetone at 50°C for 10 minutes, plus 5 more minutes in methanol. Finally, the samples were dried using a nitrogen-gas pistol.

Figure 2.1: Schematic of a finished device. Left: Side-view diagram of the device. Right: Nomarsky microscope picture of a finished diode.

Ohmic contact A photolithography process is used to define circular patterns in the sample surface, after which a multilayered metal deposition is performed. Ti/Al/Ti/Au are evaporated with thicknesses of 200/1000/400/550 Å. This recipe was used because of its great success during previous studies ([133]) and the expertise in the deposition gained during them. After some issues were found during the bonding step, the last Au layer thickness was increased to 2500 Å in order to increase adherence of the bonding thread.

Contact annealing After the lift-off process, a thermal annealing is performed to allow the metals to diffuse into the semiconductor, improving the electrical characteristics of the contact. A 1 min annealing at a temperature chosen to be about 20°C below the growth temperature is performed in a Nidron environment (95% H₂, 5% N₂).

Schottky contact + H₂O₂ treatment Right after the thermal annealing, another lithography step is performed to mark the complementary pattern on the device surface. After it, the resist is hardened by heating it, so it does not degrade during the H₂O₂ treatment. This process, needed to improve the rectification properties of the finished devices [100], consists on the immersion of the sample in boiling H₂O₂ at 100°C. Immediately following the treatment, the sample is loaded in vacuum for the deposition of a 100 Å-thick Au layer, which is semi-transparent, allowing for both electrical and optical measurements. The diameter of this contact can be chosen between 100, 200 and 400 μm, although during this thesis only the 200 μm devices have been used.

Contacts After the lift-off of the Schottky contact, a third lithography step (this one optional) can be performed, to mark a pattern for an electric contact, with two different geometries to be chosen. The choice for this thesis was the "Pac-Man" style, depicted in figure 2.1-right, that leaves the center of the device completely exposed to illumination. A 1500 Å Au layer is used for this step.

Bonding In order to be able to perform temperature-dependent measurements, samples should be bonded onto a TO-8 holder. Since the substrates used for heteroepitaxy are conductive, in order to maintain isolation from the instrument ground, a sapphire layer was introduced between the TO and the sample. Due to the different thermal expansion coefficients between the layers, a special resin had to be

used, which is capable of maintaining viscosity down to cryogenic temperatures. Bonding itself was tried both using the "ball-method" and the "wedge-method", which degraded the IV characteristics of the diode.

2.2 Current-Voltage characteristics

The first characterization step once the devices are finished, is the measurement of the current-voltage (IV) curves. By doing so, the quality of the device is easily obtained, with information about the leakage current and the device resistance. Additionally, in samples where usually many diodes are available, the most representative ones can be chosen for longer measurements (such as DLTS/DLOS), saving time.

As was explained in chapter 1, metal-semiconductor junctions (Schottky diodes) change their behavior depending on the applied bias. Summarizing, there is a region where the energy barrier is reduced (forward bias), allowing for the conduction of current between the metal and the semiconductor. On the other hand, under the reverse bias regime, the band bending and thus the barrier height increase. By changing the voltage and measuring the current that flows through the device, several parameters can be obtained: the barrier height (Φ_b), ideality factor (n), series resistance (R_s) and contact resistance (R_c).

Considering that in an ideal Shottky diode the current density can be written as:

$$J = J_s \left[e^{(qV/nkT)} - 1 \right] \quad (2.1)$$

where the saturation current (J_s) is given by

$$J_s = A^* T^2 e^{(-\Phi_b/kT)} \quad (2.2)$$

being A^* is the effective Richardson constant for thermionic emission, dependent on physical constants and the effective mass as:

$$A^* = \frac{4\pi q m^* k^2}{h^3} \quad (2.3)$$

It is straightforward that from the "ideal" part of an IV scan, both barrier height and ideality factor can be obtained by simply fitting the log plot of the JV curve under direct bias. Having these values, the difference from ideality will be given by:

$$\frac{dV}{d(\ln I)} = R_s I + n \frac{kT}{q} \quad (2.4)$$

Therefore, by obtaining the difference between the ideal and the measured values for the non-linear region of the scan, the series resistance is also easily calculated. This R_s is really helpful understanding the differences in material resistivity from a device point of view, and has proved useful on the studies with N-doped ZnO.

The last value under consideration, the contact resistance, can also be calculated from the measured curves:

$$\rho_c = \left(\frac{\partial V}{\partial J} \right)_{V=0} \quad (2.5)$$

The calculation of all these parameters from the experimental results has been automatized by a home-made LabVIEW routine that largely simplifies the selection of the

linear and R_s regions of the curve. Therefore, fastest results are obtained and more devices can be analyzed.

It is important to mention that although some devices used during this thesis are indeed MIS diodes, because of the H_2O_2 treatment, they show good rectification. This is explained from the fact that the insulating layer is indeed very thin, and tunneling currents occur under direct bias conditions. Therefore, the processed devices behave as Schottky diodes while benefiting from the passivation of the surface.

2.3 Capacitance-Voltage profiling

In chapter 1, the capacitance-voltage (CV) profiles both for Schottky and MIS devices was thoroughly explained, and related to the intrinsic parameters of the material from which the device is made off. By modulating the depletion region during voltage sweeps, information about the doping profiles of the semiconductor can be obtained. This section will begin by explaining the experimental measurement of the junction capacitance, followed by the CV profiling technique and analysis of the obtained data.

2.3.1 Measurement of a junction capacitance

In the previous chapter, capacitance was defined as the ability of a body to store electric field. Schottky and MIS structures behave as devices with two conductor plates inside, where one of them stores a charge $+q$ and the other one $-q$. In this situation, an electric field is generated in the dielectric region between the plates, being the capacitance described by the equation:

$$C = \frac{q}{V} \quad (2.6)$$

Where V is the reverse voltage applied to the junction.

For the case where both plates are parallel, the electric field remains constant, and equation 1.7 can be applied. In the previous chapter the capacitance operation of a reverse biased semiconductor junction was discussed, leading to equation 1.40, which describes the capacitance transients generated after a filling pulse.

Using basic circuit theory, the current that circulates through a capacitor is given by:

$$I(t) = C \cdot \frac{dV}{dt} \quad (2.7)$$

Which in the frequency domain can be written as:

$$I(\omega) = j\omega V \cdot C \quad (2.8)$$

Or:

$$V(\omega) = \frac{I}{j\omega C} = I \cdot Z(\omega) \quad (2.9)$$

Where $Z(\omega)$ is the impedance measured by the equipment.

It is worth noting that the current $I(\omega)$ and voltage terms $V(\omega)$ from equations 2.8 and 2.9 refer to the values measured by the equipment from the two external (metallic) terminals of the device under test. Due to the physical geometry of the planar devices used, the measured value of $I(\omega)$ should contain all the capacitive current exploring the depletion region, which is in-quadrature with the sinusoidal voltage $V(\omega)$ applied to

2.3. CAPACITANCE-VOLTAGE PROFILING

this depletion region. This displacement current occurs 90 degrees in advancement with respect to the sinusoidal voltage ($V(\omega)$), and can have an accompanying current which is in-phase with $V(\omega)$, coming from any conductive mechanism shunting the depletion region.

However, this does not pose a problem, since the measured voltage between the device terminals is the sinusoidal voltage $V(\omega)$ applied to the depletion region. Therefore, the synchronous demodulator of the impedance analyzer or lock-in amplifier will have access to all the information needed to yield the true capacitance value (C) from equation 2.9.

Added to C , the demodulator (fig. 2.2) will return the value of any resistance (R) or conductance ($G = 1/R$) shunting C at the probing frequency. This fact arises from the orthogonality of these two currents (displacement and conduction ones) created in the depletion region by $V(\omega)$.

Thus, when all the sinusoidal voltage measured between terminals ($V(\omega)$) is applied to the depletion region, the correct value for the capacitance is obtained, as well as its transient behavior. The problem arises when the voltage $V(\omega)$ measured between terminals is not applied entirely to the depletion region. This means the existence of problems to electrically access the depletion region or that an unexpected impedance (generally resistive) exists in series with the depletion region under study.

This effect could be the result of an ohmic contact becoming highly resistive by freezing, or because of an access (bulk) region decreasing its conductivity (because of intense compensation or an MIS behavior). Therefore, it is common to consider a resistance R_s in series with the depletion region region. Since this better describes the physical nature of the device under measurement, the analysis is described in terms of impedance, which considering the series resistance, is given by:

$$Z(\omega) = \frac{V}{I} = R_s + \frac{1}{j\omega C} \quad (2.10)$$

Where the capacitance-dependent term relies in the imaginary part of the equation, which can be also written in a fasorial way:

$$\vec{Z}(\omega) = \left| \vec{Z} \right|_{\varphi} \quad (2.11)$$

Where the module and phase are given by:

$$|Z| = \sqrt{\Re^2(Z(\omega)) + \Im^2(Z(\omega))} = \sqrt{R_s^2 + \omega^2 C^2} \quad (2.12)$$

$$\varphi = \arctan\left(\frac{\Im(Z(\omega))}{\Re(Z(\omega))}\right) = \arctan\left(\frac{\omega C}{R_s}\right) \quad (2.13)$$

From equations 2.12 and 2.13, it can be observed a big dependence of both terms with frequency, capacitance and series resistance. Also, noise will be added to the measurement, coming from the equipment, cables, etc. Ideally, the series resistance should be as small as possible, so the dominant factor is capacitance, but this is not always the case, depending on the samples and the equipment used.

There are several techniques available for capacitance measurements, though not all of them are applicable, due to the specific characteristics of transient operation. The simplest way of measuring capacitance is by charging and discharging the capacitor, analyzing the rise time in order to obtain the capacitance. This technique is not useful

CHAPTER 2. CHARACTERIZATION AND PROCESSING TECHNIQUES

for the purpose of this thesis, as the semiconductor capacitance depends on voltage and has its own transient operation.

A more sophisticated way of measuring capacitance is the excitation of the capacitor with an AC voltage, generating an equivalent AC current, proportional to the capacitance present at the circuit. This is the approach used by most commercial equipment.

The current generated is given by:

$$I(\omega) = \frac{V(\omega)}{Z(\omega)} \quad (2.14)$$

Which has two components: one proportional to the series resistance (real part) and the other one to the frequency and the capacitance (imaginary part). In order to make accurate measurements, both terms must meet $R_s \ll \frac{1}{\omega C}$, so the impedance depends mainly on the imaginary part. Normally, this is achieved by reducing the frequency, when possible.

For the purpose of measuring an AC current, it is normally converted into a voltage, and then measured with some specific circuitry. In the case of capacitance measurements, the AC signal is filtered, so only the probe frequency is analyzed, thus reducing noise and other parasitic effects. This can be achieved with common bandpass filters, but in capacitance meters this filtering operation is implemented using demodulators, as shown in figure 2.2.

Figure 2.2: AC signal demodulator.

In order to explain the demodulation process, first it has to be described how the frequency domain signal previously obtained in equation 2.10 behaves in the time domain. The time domain expression is given by:

$$I(t) = \Re [I(\omega) \cdot e^{j\omega t}] \quad (2.15)$$

Where:

$$I(\omega) = I_{\Re}(\omega) + jI_{\Im}(\omega) \quad (2.16)$$

and

$$e^{j\omega t} = \cos(\omega t) + j \sin(\omega t) \quad (2.17)$$

Operating, in-phase and quadrature components are obtained:

$$I(t) = I_{\Re} \cos(\omega t) - I_{\Im} \sin(\omega t) \quad (2.18)$$

As it can be observed in equation 2.18, in-phase and quadrature are also proportional to the real and imaginary part of the Fourier transform of the signal.

At the demodulator, this signal is multiplied by a *cosine* tone, at the same frequency, resulting a signal:

$$Y(t) = \frac{1}{2} I_{\Re}(t) + \frac{1}{2} [I_{\Re}(t) \cos(2\omega t) + I_{\Im}(t) \sin(2\omega t)] \quad (2.19)$$

This signal has components around DC, and components at twice the operation frequency. It is obvious that by low-pass filtering, only the term proportional to $I_{\Re}(t)$ remains.

Similarly, by multiplying the signal by a *sine* factor, the quadrature term from equation 2.18 remains. Also, it is worth mentioning that at every commercial equipment, this filtering operation also multiplies the signal by two, thus compensating the energy lost by the high frequency components.

Now that these components are separated, it can be easily observed that they represent the resistance and the capacitance proportional terms from equation 2.10. Obtaining the capacitance of the device under test is now a straightforward operation, having only to multiply the quadrature (imaginary) voltage component by a constant factor, dependent on the measurement parameters, as described by:

$$V(t) = G_{IV} \cdot \frac{V_{rms}}{Z(t)} = G_{IV} \cdot V_{rms} \cdot [R_S^{-1} + j\omega C(t)] \quad (2.20)$$

Where G_{IV} is the current-voltage conversion gain (normally in the range $10^4 - 10^6$) and V_{rms} is the *rms* (root mean square) value of the probing AC signal. Separating real and imaginary terms:

$$V_{\Re}(t) = \frac{G_{IV} V_{rms}}{R_s} \quad (2.21)$$

$$V_{\Im}(t) = G_{IV} \omega V_{rms} \cdot C(t) \quad (2.22)$$

$$C(t) = \frac{V_{\Im}(t)}{G_{IV} \omega V_{rms}} = K_C \cdot V_{\Im}(t) \quad (2.23)$$

Being obvious that the constant factor is given by:

$$K_C = (G_{IV} \omega V_{rms})^{-1} \text{ (F/V)} \quad (2.24)$$

Normally, in commercial equipment, all the steps explained are integrated into a single piece of hardware. Also, capacitance measurements can be carried out using the instrumentation that is usually found at a research laboratory. A function generator can be used to generate the AC signal that is injected in the sample. Then, the current is measured using a lock-in amplifier, that extracts the in-phase and quadrature components of the signal. Both approaches have been used during this thesis.

Figure 2.3: Doping-depth profile obtained from CV measurements at 1 MHz for two ZnO samples.

2.3.2 Capacitance-Voltage profiling

Recalling eq. 1.7 from chapter 1, and considering the incremental charge added by the AC signal, it can be written as:

$$C = qAN(W) \frac{dW}{dV} \quad (2.25)$$

Or from the carrier concentration point of view as:

$$N(W) = \frac{2}{qK_s\epsilon_0 A^2} \left(\frac{d(1/C^2)}{dV} \right)^{-1} \quad (2.26)$$

Experimentally, the derivative term is calculated from the slope at each voltage point, creating a carrier concentration vs. depth profile. Fig. 2.3 shows an example profile for undoped ZnO samples.

As mentioned in the previous section, there is a dependence of capacitance with frequency, coming from the relative intensity between the real and imaginary parts of the current measurement. However, from a physical point of view, there is an additional effect of the probing frequency on the obtained results, especially in samples with a large number of compensating centers. If the probing AC signal is too fast, the volume of the space charge region will be unable to follow the signal. That is, either N_D^+ or N_A^- or none will correspond to the fully ionized donor or acceptor states, respectively. Therefore, the apparent carrier concentration will be shifted from its steady state value. During this thesis, for highly compensated samples, the frequency had to be reduced from 1 MHz to 10 kHz to be able to measure the real capacitance of the devices.

There is another limitation to the spatial resolution of the technique, mainly in abrupt doping profiles (for example, in heterostructures or non-homogeneous doping), coming from the Debye screening effect, which measures the distance over which the free charge is screened, given by:

$$L_D = \sqrt{\frac{kTK_s\epsilon_0}{q^2N}} \quad (2.27)$$

A thorough report on the Debye length limitations on CV profiles can be found on [58]. Lastly, the voltage (and thus the depth) that can be applied to the device will be limited to the dielectric breakdown of the material. If the electric field created by the applied voltage reaches values beyond that limit, the device will be irreversibly broken.

2.4 Deep Level Transient Spectroscopy

As it has been explained, the purpose of DLTS purpose is the measurement and characterization of deep levels in semiconductor materials. First, the technique will be described, recalling some of the results from the preceding sections. Finally, a brief explanation of the different parameters that can be modified for a DLTS scan, and how they affect the obtained spectra, is presented.

2.4.1 The technique

DLTS was first described in the mid 1970's by Lang *et al* [68]¹. Here, it will be explained in its original form, recalling the theory from the sections above. There exist modifications to the original form, as techniques have evolved and improved. These differences will be explained at the end of this section.

In the first chapter the transient operation of a semiconductor junction was thoroughly described. DLTS depends on that theoretical description in order to extract the trap parameters from the measurements.

Under reverse bias operation, any semiconductor junction will show a space charge region in the lightly doped side, with a depth given by equation 1.3. After applying a filling pulse, the charge trapped at the deep levels is thermally emitted, as shown by equation 1.40, being the emission rate described by equation 1.34.

The idea beyond the DLTS technique is that it has to be capable of resolving the energy and defect concentration of unknown traps, fast, with a high resolution and in a noisy environment. Direct analysis of capacitance transients lacks most of these attributes, as transients are only maximum for a given temperature (unknown before the measurement), and they might be recorded with high resolution, being necessary complex and expensive equipment, as well as time and data storage. Thus, DLTS was developed, based on the idea of correlation and signal mathematics, obtaining the spectra in real time, while the measurement is running.

There exist different correlation techniques that can be applied to the resolution of these transients. Among all the different signal processing theories that can be applied to DLTS, the most commonly used ones are:

Double-boxcar DLTS. It is the simplest and original form of DLTS measurements, based on the subtraction of two different time points in the capacitance transient. By doing so repeatedly in temperature, the typical DLTS spectra are obtained. This is also called the "rate-window" method, since the target emission rate at which the transient is obtained was originally called by Lang a Rate Window (RW).

Lock-in DLTS. It is based on the Fourier analysis of repetitive signals, using a lock-in amplifier as a one-component tuned Fourier analyzer. It has a very good signal-to-

¹An interesting short paper about the genesis and history of the technique was published years later by the author, and can be found in [69].

Figure 2.4: Transients for various temperatures.

noise ratio, but only one rate window can be analyzed on each temperature scan, and phase and frequency tuning are critical.

Correlation DLTS. It is based on signal processing theory, which states that the optimum filter is the noise-free signal itself. The filtering is done by multiplying the measured transient by a test exponential. It has found not much application, as it requires baseline restoration, as well as modifications to the exponential with temperature.

Laplace DLTS. Based on the techniques already described, it analyzes the transients using their Laplace Transform. It gives large signal-to-noise ratios, but requires an off-line processing and complex computer software [24].

Fourier DLTS. Also based on signal processing theory, it uses the Fourier Transform of the transient signals to extract their parameters. It gives very good results, but requires complex software systems [50, 150].

For this thesis, double-boxcar (DB-DLTS) and Fourier DLTS (FDLTS) have been developed and used, and will be described in the following paragraphs.

2.4.1.1 Double-Boxcar DLTS

In DLTS, a signal is generated by subtracting the transient capacitance at a given temperature at two points in time t_1 and t_2 . In figure 2.4, it can be observed how ΔC for the capacitance transients vary with temperature.

Mathematically, the DLTS signal is given by:

$$S(T) = \frac{\Delta C}{C_\infty} = \frac{[C(t_2, T) - C(t_1, T)]}{C_\infty(T)} \quad (2.28)$$

This signal is divided by the steady-state capacitance, in order to normalize all of the transients. Also, it makes the measurement independent of the baseline. This subtracting operation is often called *Double Boxcar DLTS*, as it was initially implemented using boxcar averagers. Nowadays, all the signal processing is computerized, as it allows filtering and further data manipulation, as well as integration within the control system and storage.

It is also important to note that this difference is positive for the case of majority carrier emission, as the capacitance transients increase with time. In the case of minority carrier traps, the DLTS signal will be negative.

For the exponential transients already described, the DLTS signal is:

$$S(T) = \frac{\Delta C_0}{C_\infty} \cdot \left[e^{-t_2/\tau} - e^{-t_1/\tau} \right] \quad (2.29)$$

It is obvious that this difference is maximum when the time constant of a trap (the inverse of the emission rate) is equal to the time difference. This time difference is called a Rate Window, and is one of the main adjustable parameters in a DLTS measurement.

By differentiating equation 2.29 with respect to τ and equaling to zero, the value that makes this signal maximum is given by:

$$\tau_{max} = \frac{t_2 - t_1}{\ln(t_2/t_1)} \quad (2.30)$$

The values for t_1 and t_2 can be chosen in different ways:

1. Fix t_1 and vary t_2
2. Fix t_2 and vary t_1
3. Make $\beta = t_2/t_1$ constant²

Methods (1) and (2) are not normally used, because DLTS peaks change both in shape and size. Using method (3) is preferred, as it maintains $\ln(\beta)$ constant, and the resulting peaks have nearly the same size and shape, varying only its position.

Now, for every value of t_1 , there is a peak maximum for each trap, as its emission rate (e_n , given by equation 1.34) is equal to the desired Rate Window.

It is obvious that by only acquiring some points of a transient, and substracting them, a spectra is generated, avoiding full recording of all transients. It will be explained in the next section how to extract the trap parameters from the spectra given by a DLTS measurement.

2.4.1.2 Fourier-transform DLTS

From signal processing theory, it is known that any signal can be transformed into the frequency-domain using several of the available transforms. During this thesis, the Fourier-transform DLTS was implemented, following mainly the paper by Weiss *et al* [150]. When applying the Fourier-transform to a waveform, a series of coefficients of the form³ is obtained:

$$c_n = \frac{1}{T_w} \int_0^{T_w} f(t) e^{-jn\omega t} dt \quad (2.31)$$

where T_w is the waveform duration, $\omega = \frac{2\pi}{T_w}$ and n is the order of the obtained coefficient. These coefficients are imaginary, giving as a result the sine (a_n) and cosine coefficients (b_n) of the Fourier series as:

$$c_n = 1/2 (a_n - jb_n) \quad (2.32)$$

²This parameter is also called α , r or Δt among literature.

³During this thesis, the imaginary unit will be represented as j . This is common practice in engineering, in order to avoid confusion with the representation of currents in time-domain, where the letter i is used.

CHAPTER 2. CHARACTERIZATION AND PROCESSING TECHNIQUES

However, when signals are digitized, the Discrete Fourier Transform (DFT⁴) is performed, obtaining coefficients of the form:

$$F_n = \sum_{k=0}^{N-1} f_k e^{-2\pi j n k / N} \quad (2.33)$$

being N the number of samples obtained for the waveform and f_k the k -th sample in that digitized waveform. It is important to place attention to the fact that any of the coefficients have information from the whole transient, thus reducing the effect of noise. These discrete DFT coefficients relate to the analytical Fourier transform for the original waveform as:

$$F_n = N c_n \quad (2.34)$$

Computationally, a very efficient algorithm for the calculation of the DFT coefficients is available, called the Fast Fourier Transform, which is implemented in most of the mathematical software used in laboratories. Therefore the implementation given by LabVIEW was instantiated in the software routines that perform the FDLTS measurements in the lab, as will be described in a later chapter.

Recalling the expression for an exponential function, similar to those coming from the deep level emission:

$$f(t) = A e^{-(t+t_0)/\tau} + B \quad (2.35)$$

where t_0 is the start of the transient, A is the transient amplitude, B is the offset and τ is the time constant of the transient (it can be written to use emission rates, considering $\tau = 1/e_n$). For these type of functions, the a and b coefficients can be obtained from:

$$a_n = \frac{2A}{T_w} e^{-t_0/\tau} \times \left(1 - e^{-T_w/\tau}\right) \frac{1/\tau}{1/\tau^2 + n^2\omega^2} \quad (2.36)$$

$$b_n = \frac{2A}{T_w} e^{-t_0/\tau} \times \left(1 - e^{-T_w/\tau}\right) \frac{n\omega}{1/\tau^2 + n^2\omega^2} \quad (2.37)$$

Usually, coefficients of orders larger than $n = 2$ are very low in magnitude, providing no new useful information. During this thesis, only $n = 1, 2$ have been used to calculate the transient parameters. Before obtaining any useful value, the DFT can check whether the input waveform is exponential, thus discarding the values for which it is not (from the physical point of view, this will mean that for that particular temperature, there is no emission from deep levels). Operating on the values obtained from eqs. 2.36 and 2.37:

$$a_2 < a_1 < 4a_2 \quad (2.38a)$$

$$b_2/2 < b_1 < 2b_2 \quad (2.38b)$$

$$\frac{b_1}{a_1} \frac{a_2}{b_2} = \frac{1}{2} \quad (2.38c)$$

⁴Here, the acronym is the same as for Density Functional Theory, although the context helps disambiguate the meaning.

Figure 2.5: Example Arrhenius plot for the E3 level in m-ZnO measured by DB-DLTS (solid circles) and FDLTS (open triangles).

Once the validity of the Fourier series is checked, the emission rate for the transient can be easily obtained using the expressions given by

$$\tau(a_n, a_k) = \frac{1}{\omega} \sqrt{\frac{a_n - a_k}{k^2 a_k - n^2 a_n}} \quad (2.39a)$$

$$\tau(b_n, b_k) = \frac{1}{\omega} \sqrt{\frac{k b_n - n b_k}{k^2 n b_k - n^2 k b_n}} \quad (2.39b)$$

$$\tau(a_n, b_n) = \frac{1}{n\omega} \frac{b_n}{a_n} \quad (2.39c)$$

From eq. 2.39 it can be observed how the emission rate is obtained without needing to know neither amplitude nor offset. For the purpose of FDLTS, this value will yield directly the emission rate at a given temperature, without the need for RW or peak analysis. Therefore, an Arrhenius plot can be obtained "live" during the scan. Additionally, many more data points are calculated than with the RW method, giving higher confidence levels on the fits. Fig. 2.5 shows this result, with much more points available in the FDLTS measurement compared to the same level (actually, obtained on the exact same temperature scan) analyzed by DB-DLTS.

Also, the amplitude of the transients, and thus the level concentration can be obtained from the coefficients from eq. 2.37 as:

$$A = \frac{T_w}{2} b_n \frac{e^{t_0/\tau}}{1 - e^{-T_w/\tau}} \frac{1/\tau^2 + n^2 \omega^2}{n\omega} \quad (2.40)$$

Recalling eq. 1.38, it is straightforward that the concentration for the trap can be obtained from the amplitude of the transient, given by eq. 2.40.

2.4.2 Parameter extraction

Once a DLTS spectra is obtained, the objective is to extract the trap parameters from it. Figure 2.6 shows an example of a DB-DLTS spectra for two simulated traps measured under different Rate Windows.

Figure 2.6: Example DB-DLTS spectra for various Rate Windows.

For a given Rate Window signal, and for each peak, the position and height can be extracted.

Remembering equation 1.36:

$$\tau_n = e_n^{-1} = \frac{e^{\frac{\Delta E}{kT}}}{\sigma_n \gamma_n T^2} \quad (2.41)$$

Substituting in equation 1.35 and taking the natural logarithm results in:

$$\ln(\tau_n T^2) = \frac{\Delta E}{kT} - \ln(\sigma_n \gamma_n) \quad (2.42)$$

From this equation, it is obvious that by using the peak temperature for a given emission rate (time constant or Rate Window), it is possible to generate an Arrhenius plot of $\ln(T^2/e_n)$ versus $(1/T)$, as it can be seen in figure 2.7. By linear fitting the data, an intercept and slope are obtained. This process is independent of the measurement method, whether it is DB-DLTS or FDLTS. Indeed, the measurement routine implemented in the lab performs both analysis simultaneously.

Activation Energy

Using equation 2.42, it can be observed that the slope for a set of (T, e_n) pairs give the ΔE term. As it is normally plotted against $1000/T$ instead of $1/kT$, the activation energy for a given trap yields:

$$E_a = \Delta E = E_C - E_T = 1000 \cdot k \cdot slope \quad (2.43)$$

Where k is the Boltzmann constant ($k = 8.617 \cdot 10^{-5}$ eV/K).

Effective cross section

Also from equation 2.42, the effective cross section for a given trap can be derived using the intercept of the Arrhenius plot.

Figure 2.7: Arrhenius plot for the spectra in figure.2.6

$$\sigma_n = \frac{e^{\text{intercept}}}{\gamma_n} \quad (2.44)$$

Where γ_n is a parameter dependent on the material, given by:

$$\gamma_n = 3.25 \times 10^{21} \times m_n^* \text{ (cm}^{-2}\text{s}^{-1}\text{K}^{-2}\text{)} \quad (2.45)$$

The analysis of the effective cross section from Arrhenius plots is sometimes difficult, as there are lots of limiting factors that generate scattering in the obtained data. Anyway, the most important one is that often the cross section for a trap is also temperature dependent, as given by:

$$\sigma_n = \sigma_\infty e^{-E_\sigma/kT} \quad (2.46)$$

This Boltzmann exponential dependence also affects the activation energy measurement, but not in such a factor as it does with the obtained cross section.

Also, data scattering coming from noise, equipment errors and other sources largely affect this value. This value is then a factor in an exponential function. All these irregularities lead to errors as big as 50% of the measured value.

Concentration

Using equation 1.40 for the DLTS signal, it leads to:

$$\delta C = \frac{C(t_2) - C(t_1)}{C_\infty} = \frac{N_T}{2N_D} \left[e^{-t_2/\tau} - e^{-t_1/\tau} \right] \quad (2.47)$$

It is important to mention that this DLTS signal does not give the maximum amplitude of a transient, but the maximum difference between two points. Thus, a correction on the measured DLTS signal will be needed:

$$r = \left[e^{\left(\frac{\ln \beta - 1}{\beta - 1} \right)} - e^{\left(\frac{\ln \beta - 1}{1 - \beta - 1} \right)} \right]^{-1} \quad (2.48)$$

For FDLTS, this r parameter will be unity, not needing further correction. Considering all the previous expressions, the trap concentration, obtained from the DLTS spectra will be:

$$N_T = 2N_D r \frac{\delta C_{max}}{C_\infty} \quad (2.49)$$

Measurement errors

As with any experimental technique, DLTS is sensitive to measurement errors and uncertainties in the obtained parameters. The first and obvious source of uncertainty will be the resolution of the equipment, being this especially important for the calculation of the concentration, since an accurate measurement of the $\Delta C/C_0$ value is necessary. Moreover, each RW is affected differently by the electrical noise, obtaining a different peak height for each one of them. Therefore, a range in the trap concentration will be obtained, which can be minimized by performing the measurement with a large number of different RWs.

For the case of the parameters obtained from the Arrhenius plot (E_a and σ_n), the uncertainties will come from the dispersion of the points in the linear fit. Usually, the software used to perform this operation yields a confidence value for both the slope and intercept. Since E_a is calculated by simple multiplication of the slope by a constant factor, a maximum and minimum value can be computed, obtaining an $E_a \pm X \text{ eV}$ range. The exponential character of the cross section will yield a $\sigma_n \times \div Y$ kind of range. It is worth mentioning that by using FDLTS, because of the extended number of available points in the Arrhenius plot, the uncertainties can be reduced to the minimum.

2.4.3 Operation

The operation of a DLTS system is very simple, and consists on the next steps:

1. Reach the initial temperature. Normally, DLTS scans are carried out starting at a very low temperature, increasing it at each step. This is done because heating is faster than cooling, and most cryostats have to get stabilized before temperature measurements are accurate enough.
2. Reverse-bias the junction, so a space charge region is generated.
3. Apply a short filling pulse, so the existing traps are filled.
4. Reverse bias the diode again.
5. Measure the capacitance transient following the filling pulse. After this step, normally a voltage signal proportional to the junction capacitance is recorded, so it can be processed at the next step.
6. Obtain some parameters from the transient. Using any of the variations mentioned above, the DLTS signal is generated and stored. Also, the transients can be stored for further analysis. In all the modern DLTS systems, this signal processing is computerized, so complex algorithms and filtering operation can be implemented.

7. Repeat steps 2-6 among all the desired temperature range. Normally, the temperature is increased gradually, so the measured value represents the actual junction temperature, and the DLTS signal measured gives the real trap distribution among the sample.

Equipment

Depending on the DLTS variation chosen, different equipment is present, although almost all of the implementations need the same basic blocks of equipment. The details about the implementation at the ISOM laboratories will be given in chapter 4, with a complete description of the existing equipment.

In order to vary the temperature, a cryostat is needed. Depending on the temperature range desired (it has a strong relationship with the energies that can be measured), there are many commercial cryogenic systems. In general, the most popular ones are the closed cycle helium cryostats, that are capable of reducing temperature to near 10 K, and the immersion nitrogen cryostats, which only allow measurements starting at around 90 K.

Both cryogenic systems work primarily the same way. The sample is introduced in a vacuum chamber, where only one metal part is cooled. Between this cold finger and the sample there is a heating resistance, controlled by an external temperature controller (normally using a feedback control cycle), and a temperature probe (can be a thermocouple or a specific diode). By increasing the current that circulates among the heating resistance, an increasing temperature is generated, thus increasing the sample temperature.

The filling pulse is generated with one of the analog outputs from the DAQ board in the case of 1 MHz measurements, and using a function generator for lower frequencies. It is important to mention that the capacitance measurement systems normally have slow responses (slew rate), so the filling pulse slopes have to be tuned in order to not overload the measurement equipment.

Once the filling pulse is generated, it has to be added to the probe AC signal, so it can be injected onto the sample. This can be achieved using specific circuitry, normally signal couplers and adders. There have been many approaches published for these coupling bridges, specially at the beginning of DLTS measurements, when no high frequency integrated circuits were available. Some examples of specific bridges are found among published literature [92].

Although specific circuitry can be used, the AC signal and its addition to the filling pulse is usually carried out using commercial capacitance meters, as the Boonton model 72 and its modern version 7200B. This equipment has the capability to generate the probe signal, add an external filling pulse, and measure the capacitance for the sample, generating a proportional voltage signal that can be easily measured using conventional Digital Storage Oscilloscopes (DSO) and DAQ boards. In the case of low frequency measurements (using a lock-in amplifier), a custom signal adder/buffer is used to adapt and add the AC and DC components of the probe signal.

Once a voltage signal proportional to the capacitance is obtained, it has to be recorded using any available system (multimeters, DSO or signal acquisition systems). Although initially DSOs were used on the DLTS system at ISOM, during this thesis a powerful DAQ system was introduced, as will be thoroughly explained in chapter 4.

At this step, the data is transferred to the computer, which will also measure and control the temperature step. Inside the computer lives a specific software piece, developed using the LabVIEWTM environment, which implements the instrument control and

data analysis necessary to obtain DB-DLTS and FDLTS spectra.

2.4.4 Parameter choice

As it has already been described, there are many different parameters that can be varied during a DLTS measurement. Here, the most important ones will be explained, in order to give a general overview of a measurement preparation, and how to analyze the obtained data.

Fill pulse (time and voltage)

During the theory at the beginning of this chapter, it was always assumed that during the filling pulse all traps were completely filled, thermally emitting those carriers after a reverse bias was applied again. This is only an approximation to explain and describe the exponential thermal emission rates, but does not completely represent reality.

During the filling pulse, traps will be filled with carriers following the capture rate defined in chapter 1. Therefore, if the pulse is too narrow, some traps will not be completely filled, as they may not have been given enough time to do so. Measurements varying the fill pulse width are normally carried out, to obtain the filling behavior of the trap, being able to differentiate between point and extended defects [43].

Also, the fill pulse amplitude is of great importance. It can be varied so only some chosen traps are filled. There are mainly two cases:

- Reverse bias fill pulse. It reduces the applied voltage, but maintaining the junction under reverse operation. This way, as it has been already described, the depletion width is reduced, filling the traps present only on the region undepleted. These traps will only be filled with majority carriers, as no minority carrier injection will occur.
- Forward bias fill pulse. In this case, the device is driven onto forward bias, thus injecting both minority and majority carriers. This way, both type of traps can be measured. However, this is only applicable to pn junctions, since for Schottky diodes, the potential barrier present at the minority carrier band will impede the injection of such carriers, despite of the biasing point.

Reverse voltage

In the first chapter, it was pointed out that the depletion width for a reverse biased junction depends on the magnitude of the reverse bias voltage. It is obvious, though, that by varying this voltage, the depth at which the material is scanned can be chosen. This is a very good way of analyzing structural defects with depth resolution.

If the depletion region varies largely during temperature scans, the previous assumption may be wrong, since very different volumes of the material will be probed. To circumvent this issue, Constant Capacitance DLTS can be implemented. This technique uses a feedback circuit to maintain the capacitance constant, by varying the applied voltage. Its main application is the profiling of large generation-recombination centers, and measurements in samples where $N_T \geq 0.1N_D$.

Rate windows sets

Rate windows are the name of the emission rate pre-fixed, at which a maximum in the DLTS signal will be produced. From equation 1.34 it can be observed that this parameter decreases with temperature (the generated transient is "faster"). Thus, DLTS peaks will move onto higher temperatures as a larger (faster) Rate Window set is selected. This allows selecting the temperature range at which the measurement will be carried out, based on an initial scan, or depending on the equipment available at the laboratory. This also applies to FDLTS, where measuring with different T_w can shift the levels in temperature, avoiding noisy regions or overlapping of emission from different levels.

It is worth mentioning that very short transients are normally difficult to measure, as the equipment normally has a given response time. Also, high frequency noise components will be of much greater importance in these short-living signals.

2.5 Deep Level Optical Spectroscopy

Following the success of DLTS after it was first published in 1974, an optical variety of the technique was presented by Chantre *et al* in 1981 [16]. It is based on the same principles and dynamics for the energy levels in semiconductor materials, only using light to force the emission of the trapped carriers. This technique is extremely powerful for the measurement of wide bandgap semiconductors, since it can access the region of the bandgap which DLTS cannot probe (which is around 1 eV from the majority carrier band). Additionally, it allows to measure acceptor-like levels (or most precisely, levels close to the VB) in n-type material.

2.5.1 Operation

Although many variations are suggested, the easiest and most common one is fairly similar to DLTS.

1. Load and align the illumination spot to achieve maximum illumination power.
2. Wait in the dark until the persistent photo-effects disappear
3. (Optional). Apply an electric fill pulse in the dark. This helps to fully let the levels capture carriers.
4. Reverse bias the junction and wait for the DLTS-like transients to pass.
5. Apply monochromatic light, during which the capacitance is recorded.
6. Record the steady-state photocapacitance plus Q-factor and conductance.
7. Repeat steps 3-6 until over-bandgap energies are reached.

Mathematically, its operation evolves from the theory presented in chapter 1. Remembering eq. 1.39:

$$\frac{dn_T}{dt} = -\sigma_n^o + \Phi n_T + \sigma_p^o \Phi p_T$$

The most straightforward result will be given by the steady state value ($t \rightarrow \infty$):

$$n_{t \rightarrow \infty} = N_T \frac{\sigma_p^o}{\sigma_n^o + \sigma_p^o} \quad (2.50)$$

This steady state trap concentration can be easily transformed onto capacitance values, which will then be recorded at different illumination energies, obtaining a steady-state photocapacitance (SSPC) spectra similar to the one depicted in fig. 2.8.

2.5.2 Parameter extraction

From the SSPC spectra both the trap energy and its concentration can be obtained, as follows, whereas for the cross sections, the transients need to be analyzed.

Trap energy

The onsets in the SSPC spectra indicate the presence of levels, which after being excited reduce or increase the amount of fixed charge, resulting in an increment or decrement of the measured capacitance. Therefore, a majority carrier trap will lead to a positive onset. Since these transitions are always defect-band transitions, they give the real trap energy (E_T), as contrary to the activation energy (E_a) given by DLTS. To get this energy, the energy position at which the onset is observed must be subtracted from the bandgap energy, as can be observed in fig. 2.8.

Concentration

In order to get the trap concentration, as long as $\Delta C/C_0 \ll 1$, the procedure will be very similar to that performed on DLTS. Just by applying

$$N_T = 2N_D \frac{\Delta C}{C_0} \quad (2.51)$$

where ΔC is the difference between the upper and lower points of the onset, the concentration for a given trap is obtained.

Optical cross section

Chantre proposed that in order to obtain values which are not mixed interactions between the hole and electron capture cross sections, eq. 1.39 could be reduced to its $t = 0$ value:

$$\left(\frac{dn_t}{dt} \right)_0 = -\sigma_n^o \Phi N_T \quad (2.52)$$

Therefore, by measuring the derivative of the capacitance transient at its beginning, the optical cross section for a level can be obtained. It is important to mention that for samples where persistent photo-effects are not negligible, the start of the transient can be heavily influenced by the previous step, thus reducing the effectiveness of this approach. Waiting for longer time periods in the dark between illumination pulses can drive the measurement impossible.

Figure 2.8: Typical SSPC spectra for a DLOS measurement on a ZnO sample.

Measurement errors

Similarly to what was exposed for the case of DLTS, DLOS is affected by measurement errors and uncertainties. In addition to electrical noise, that can largely affect the accuracy of the obtained values, there exist error sources intrinsic to the technique nature. As it has been already explained, obtaining the infinite value for the steady state measurement can be complicated if the time needed to reach a stable value is larger than the one used during the scans. Therefore, the calculated value can be lower than the real trap concentration.

Additionally, because of the need to manually position the onset energy to obtain the trap energy (E_T), a subjective error can be introduced by the researcher, especially in onsets that are coincident with the rise from a previous defect. Moreover, because of limitations from the monochromator used in the experimental setup, the minimum step that can be used is limited, with the monochromatic light not being completely monochromatic, and having illumination energies slightly above and below the configured value, which can excite traps at apparent energies below the obtained one.

2.5.3 Parameter choice

As with any experimental technique, careful selection of all the available parameters has to be performed, especially in complex and time-consuming spectroscopies as is DLOS. Repeating the measurements is difficult, since after illumination some samples can exhibit large decay times to recover from persistent photo-effects. Therefore, ensuring that every parameter is chosen optimally for the purpose of the experiment is even more crucial.

Transient time

This parameter is important mainly for SSPC measurements. Emission rates can be slow, sometimes in the order of several minutes, especially if there is a competition between capture and emission rates (which depends on the trap nature and the available states

Figure 2.9: Some of the mentioned issues with DLOS measurements. Left: dependence on the optical power. Right: persistent photo-effects in the fill pulse.

in the bands for that particular energy). Therefore, to attain truly the steady state and be thus able to obtain the true trap concentration, this value will have to be kept long.

It is good practice to perform first a scan with a large energy step, and short transient times, increasing it later to a much larger value (for example, starting with 30 sec and then measuring for 2 min). By comparing both measurements, an idea of how much the transient time will have to be increased is obtained.

However, there is another issue regarding high-purity material, where excitonic absorption plays an important role on the optical properties of the device. There, upon photo-excitation with energies close to $E_g - E_{exc}$, the conductance increases dramatically, reducing the capacitance measurement quality factor (Q). Additionally, optical systems work by letting light pass through the monochromator, filtering the higher order energies from the resulting spectra. However, this leaves some of the stray light still reaching the device. This stray light can degrade the electrical properties despite being orders of magnitude lower in intensity compared with the main illumination energy. Therefore, close to bandgap in very high quality material, shorter transient times have to be used, not to reach a saturation point in the detection circuitry and the device.

Fill pulse

Similarly to DLTS, the fill pulse has to be kept long enough so that the capacitance is allowed to reach its dark value. If not, when performing the derivative at $t \rightarrow 0$, a combination of a still-decaying persistent photo-effect and the rise due to the illumination will be measured. An example of this situation is depicted in fig. 2.9-right, where the real measured value (C'_0) and the ideal dark value (C_0) are indicated.

Optical parameters

DLOS measurements are extremely dependent on the little variations in optical flux that occur in a range of energies, such as peaks in the lamp power, grating and filter changes, etc. Additionally, the issue with the stray light already mentioned concurs, sometimes hindering the correct identification of the deep levels present in the sample. Fig. 2.9-left shows some of these problems, where the signature from traps is mixed with lamp features and grating and filter changes that create onsets similar to those coming from deep levels. A correct calibration of the system and the characterization of its emission spectra is crucial for optical spectroscopy.

Frequency

In highly compensated material, as the one which will be presented in chapter 7, the resistivity for the device can be so large that correct capacitance measurements is impossible. As it was mentioned at the section about measuring capacitance, the only way to circumvent this issue is to reduce the frequency as much as possible without destroying the signal-to-noise ratio (SNR).

Initial waiting

After the initial alignment of the signal in the measurement stage to maximize the optical flux on the device, persistent photo-effects can be induced in it. In order to allow for a correct measurement from the beginning of the scan, some time has to be let for the sample to relax to its darkness behavior. However, if a scan is to be performed at high energies, close to bandgap, this time can be reduced since at those energies the persistent effects play a smaller role on the overall shape of the DLOS spectra.

2.6 Lighted Capacitance-Voltage profiling

For the case when $\Delta C/C_0 \ll 1$ does not apply (for example, in heavily compensated material), Armstrong *et al* proposed Lighted-Capacitance-Voltage (LCV) [3] to complement SSPC measurements. Once the onsets in the SSPC spectra are identified, the energy corresponding to the trap is already available, being necessary a method to obtain the trap concentration. LCV operation principle is fairly simple. By measuring CV profiles under illumination at different energies, the contribution for each single defect level can be measured.

For example, let's consider a sample with a single level at an energy E_T . When measured in the dark, a CV profile will only have information about the ionized donor and acceptors close to the bands:

$$N_{dark} = N_D^+ + N_A^- \quad (2.53)$$

This will apply up to energies close to $E_g - E_T$. However, if the illumination energy is larger than that value, the charge trapped in the defect will be emitted, being the carrier concentration:

$$N_{h\nu} = N_{dark} + N_T = N_D^+ + N_A^- + N_T \quad (2.54)$$

Therefore, by just subtracting the obtained carrier concentration below and over the trap energy, the contribution for that single level can be calculated. This can be repeated as many times as needed for each of the onsets found in the DLOS spectra:

$$N_T = N_{h\nu} - N_{dark} \quad (2.55)$$

Fig. 2.10 shows an example set of LCV curves and their corresponding carrier concentrations for different illumination energies. It can be observed that the carrier concentration increases for larger energies, as is expected from a DLOS spectra that resembles that from fig. 2.8.

An issue that was observed, and that will be thoroughly analyzed in chapters 3 and 7 occurs when measuring MIS devices using LCV. The photogenerated carriers will then not contribute towards an increase in the carrier concentration measured using the

Figure 2.10: Example LCV measurement of a ZnO device under different illumination energies. The obtained carrier concentrations (left) and the original CV profiles (right) are shown.

standard CV profiling techniques, but will add to the inversion or accumulation layers in the device. This can shift the operation regime from depletion onto accumulation or inversion, which can be useful to assess the presence of the insulating layer.

2.7 Photoluminescence

The only purely optical technique that has been used during this thesis is photoluminescence (PL), which is a widely used spectroscopy technique. It allows to gather information about the material quality, band structure, the presence of excitons, donors and acceptors, etc, without the need to process devices. Therefore, it helps get preliminary information, on the one hand, and compare and contrast the results obtained by electrical measurements, on the other hand.

It is based on the generation of electron-hole pairs through optical excitation, followed by their radiative recombination and emission of photons of certain energy. These processes were described in chapter 1. Experimentally, the operation is fairly simple 2.11:

Temperature . Since the bandgap, non-radiative recombination and ionization of the levels present in the material depend on temperature, the samples are loaded in a cryostat with which the temperature can be controlled in a large range.

Optical excitation . By using a He-Cd laser with a lasing wavelength of 325 nm (or 3.815 eV), electron-hole pairs are generated by exciting electrons from the valence band up to the conduction band.

Carrier thermalization . The excited carriers thermalize to the band edges, excitons or defects.

Electron-hole pair recombination . Electrons and holes recombine at a given energy level creating photon emission.

By recording the energy distribution and relative intensity at the different wavelengths, a PL spectra is obtained. Each of the emission peaks, their width, relative intensity and replicas will give information about the material composition, as well as the

Figure 2.11: Schematic for the recombination processes involved in photoluminescence: (a) Excitation with over-bandgap photon energies; (b) Relaxation of the carriers to the band edge; (c) Radiative recombination of the electron-hole pair.

presence of exciton coupling (for example, with donors or acceptors), and other material-quality-related parameters. By using power-dependent measurement and temperature-dependent scans the origin of many of the peaks can be resolved. This makes it a helpful tool for the defect spectroscopist, being able to cross-check the results from electrical measurements.

Part II

Equipment and techniques development

Chapter 3

Deep level spectroscopy in Metal-Insulator-Semiconductor devices

This section is based on the published article "Deep-level spectroscopy in metal–insulator–semiconductor structures" by Kurtz, A., Muñoz, E., Chauveau, JM. and Hierro, A.

Published in the Journal of Physics D: Applied Physics 50 (2017) 065104

Reference number: [67]

Presented at the 13th EXMATEC conference, celebrated in Aveiro, Portugal between June 8-10, 2016.

Obtained the "Sociedade Portuguesa de Física" student award.

3.1 Introduction

The deep level spectroscopy techniques described in chapter 2 are powerful tools to assess the presence of electrically active defects in semiconductor materials [16, 68]. However, both DLTS and DLOS rely on the use of specific devices where a depletion region is well defined, such as in highly asymmetric p-n junctions (where the depletion region drops on the lightly doped side of the junction) or in Schottky junctions. Still, both of these devices pose great technological difficulties for many materials of current interest. First, some materials suffer from large surface carrier accumulation or conductivity, in which Schottky contacts are not feasible. This is the case of InGaN alloys, which show a high surface carrier accumulation [10], which similarly to ZnO [14] and CdO [57], impede the formation of Schottky contacts. Moreover, as it was explained in chapter 1, many wide bandgap materials present difficulties with one of the doping types, the so called doping asymmetry [156], hindering the realization of p-n junctions. Finally, and even if p-n junctions could be realized in a given material system, the requirement of having an asymmetric p-n junction with at least an order of magnitude difference in the doping level between both sides (to ensure the depletion region drops mostly on the lightly doped side), may be unreachable in material systems where the residual carrier concentration is high.

To circumvent these limitations, MIS structures are a suitable solution, since they can avoid most of the aforementioned difficulties. Therefore, by extending the knowledge

CHAPTER 3. DEEP LEVEL SPECTROSCOPY IN METAL-INSULATOR-SEMICONDUCTOR DEVICES

of DLTS/DLOS for bulk deep level analysis to MIS devices in a controlled way and by properly quantifying the new effects this insulating layer generates on the techniques, a wider range of materials could be analyzed. Moreover, not only DLTS/DLOS could be performed on MIS structures, but other techniques based on modulating the depletion region will be affected in a similar way and would benefit from such understanding. A good example of the role that an MIS structure has is ZnO, where the surface is passivated to allow the formation of a rectifying Schottky junction [15, 61, 100, 128]. In this material, as has been discussed in the previous chapters, the surface is typically treated with H_2O_2 [36, 61, 100], which induces the formation of a thin insulating layer [100]. However, even if the IV curves resemble that of a Schottky diode, there could be a hidden MIS structure that can strongly affect the capacitance transient behavior of the device, as it has been already observed in MgZnO:N measured by DLOS [66].

Early results using MIS devices for DLTS analysis mainly focused on probing interface states, pulsing the device into accumulation or inversion. Just few years after D.V. Lang first described the basis of DLTS [68], several studies came out applying the technique to insulator-based devices [18-23]. The first report by Wang et al. [147] used IGFETs to measure only interface traps, with a theoretical discussion on the procedure, which was further improved by Schulz et al. [123], and Özder et al. [104, 105] in Si MOS structures. The most thorough report on the measurement of bulk states instead of surface states, in MOS diodes, was published by Yamasaki et al. [152]. In their work, the processes of carrier emission from bulk states were analyzed, obtaining very similar expressions to those from DLTS. However, they failed to point out the similarities between the measurement processes for MIS or Schottky/p-n diodes, despite the presence of an insulating layer. Also, their model did not consider the transient effects coming from the presence of the insulator, i.e., they assumed the voltages to be constant, which is not a complete description, as it will be shown in this paper. Several years later, Nakashima et al. [101] extended that work, adding an investigation of MOS on SOI structures, describing the measurement for lock-in DLTS, but again lacking a complete study of the voltage and timing regimes in MIS devices, and the proper design of the experiments. Our work further expands and simplifies the analysis of DLTS in MIS devices, comparing the obtained spectra with that one measured in a non-insulator-affected sample, which is of great importance in materials with native insulating layers that are difficult to characterize and for the measurement of semiconductors with high carrier concentration (intrinsic or from doping), in which the design of the experiment is crucial to maximize the sensitivity of the measurement.

3.2 Theoretical Model

3.2.1 Basic MIS theory

As explained in detail during chapter 1, MIS devices show different operation modes (accumulation, depletion and inversion) as a function of semiconductor doping levels, insulator characteristics and applied bias. Depending on the operation mode, the region of the material being probed using spectroscopic techniques varies largely, and has to be taken into account when analyzing the experimental data.

Recalling the equivalent electrical circuit for an MIS structure (inset of Fig. 3.1, which resembles fig. 1.16), it can be observed that the total capacitance will be the series combination of two capacitances, the insulator capacitance (C_{ins}) and the semiconductor depletion region capacitance (C_d), as expressed by eq. 1.21, where the time dependence

Figure 3.1: Metal-Insulator-Semiconductor capacitance-voltage profile for n-type material indicating the different operation regimes. Inset: Equivalent circuit for an MIS structure in the depletion regime. Composed from figs. 1.13 and 1.16.

has been added:

$$C_{total}(t) = \frac{C_d(t) \cdot C_{ins}}{C_d(t) + C_{ins}}. \quad (3.1)$$

The MIS structure has a capacitance-voltage (CV) profile that indicates the aforementioned operation regimes (Fig. 3.1). For the purpose of material spectroscopy techniques, we will focus on the depletion regime, since it is the one that exposes the bulk material beneath the structure, so that the existing deep levels can be filled and emptied, modulating the depletion volume. Under this regime, it is important to mention that there is no significant impact of the probe frequency associated with the insulating layer, despite the effect in the limit frequency posed by the presence of deep levels for capacitance measurements [12]. Therefore, standard capacitance/impedance meters can be used (normally working at 1 MHz in order to improve the signal-to-noise ratio).

Two parameters are indicated in Fig. 3.1 that are important for understanding MIS structures operating in the depletion regime. The first one, C_{min} is reached when the depletion region width is maximum ($C_{d,max}$), just before the inversion layer is formed and no more depth modulation can be achieved [132]. It poses an effective limit on the depth that can be measured during the spectroscopy scans, and is indicated by the expression (simplification of eq. 1.14)

$$C_{min} \propto W_{d,max}^{-1} \approx \sqrt{\frac{4\epsilon kT \ln\left(\frac{N_D}{n_i}\right)}{q^2}}, \quad (3.2)$$

where N_D denotes the carrier concentration in the film.

The second important parameter is the threshold voltage (V_T) [132], which assuming an ideal MIS structure with no trapped oxide charge and no differences in the metal/oxide/semiconductor work functions is given by

$$V_T = \frac{kT}{q} \ln \frac{N_D}{n_i} - \sqrt{\frac{4\epsilon kT N_D \ln \left(\frac{N_D}{n_i} \right)}{C_i}}. \quad (3.3)$$

Both expressions show similar dependencies on carrier concentration, temperature, and the insulator capacitance. Moreover, and as it will be explained in the following section, the capacitance arising from the depletion region depends both on carrier concentration and applied voltage, being both parameters (C_{min} and V_T) modified during time as a result of carrier capture and emission processes, which are the basis for capacitance spectroscopy techniques.

3.2.2 MIS structures for deep level spectroscopy

In this section we present our model for the steady state and transient operation in MIS devices for capacitance spectroscopy techniques, which are based on fill pulses (optical, electrical or both). The analysis of the relative effects introduced by the insulating and semiconductor layers will be analyzed.

Steady state operation

Under steady state operation, the applied voltage (V_a) on an MIS structure will have to drop between the insulating layer (V_i) and the depletion in the semiconductor film (V_d) as $V_d + V_i = V_a$ (eq. 1.17).

Since the charge in the insulator and the semiconductor are the same,

$$V_x = \frac{Q_s}{C_x}; \text{ Where } x = \begin{cases} i : \text{insulator} \\ d : \text{depletion} \end{cases} \quad (3.4)$$

and accounting for Eq. 3.1, then

$$V_i = V_a \frac{C_d}{C_d + C_i}. \quad (3.5)$$

Therefore, the smaller the capacitance from the insulator is (thicker layer), the larger the voltage that drops in it. Fig. 3.2 shows the relative amount of the applied voltage (V_a) that will drop in the insulator layer as a function of its thickness for various carrier concentrations in a given sample. This graph has been generated for a material with a static dielectric constant of 8.7 (ZnO), although for materials with different dielectric constants there will only be a horizontal shift in the curves. Ideally, it is desirable that the sample is designed to operate in the lower part of the graph, in order to maximize the control over the depletion voltage by minimizing the amount of voltage that drops in the insulator. This will be generally the case for very thin insulating layers, such as those created unintentionally by means of surface treatments or oxidation processes, considering the usual range of values for dielectric constants in semiconductors and native insulators. Moreover, by proper control of the voltage drop in the depletion region (V_d), depth sensitive measurements could be carried out.

It is also important to mention that for thin insulators, and as a consequence of Fig. 3.2, samples with carrier concentrations as high as 10^{18} cm^{-3} could be measured provided that a satisfactory model is developed. As indicated above, such a high doping regime is typically inaccessible for DLTS/DLOS because of the difficulty processing Schottky diodes or heavily doped asymmetric p-n junctions.

Figure 3.2: Percentage of the applied voltage dropping in the insulator as a function of doping concentration and insulator thickness ($t_{ins} = 10, 20, 50, 100$ nm). The graph is composed assuming a static dielectric constant of 8.7 (ZnO).

Transient effects in MIS structures

From the DLTS basis described in chapters 1 and 2, it can be recalled that during the scans, samples are subjected to repeated bias square pulses. Under the transient operation following the DLTS/DLOS fill pulse, the bias time variation has to be considered and modeled accordingly. The first and most obvious transient behavior following the electrical fill pulse will be the rearrangement in electric fields inside the structure. As previously indicated, the applied voltage has to drop between the insulator and the semiconductor. However, this process is not immediate, and affects the transient operation of the structure. Since for deep level spectroscopy it is assumed that in the depletion region ($\Delta C_d/C_{d,\infty} \ll 1$), that is, the depletion width changes relatively little compared to the overall background width, the charge or discharge process due to the insulating layer can be assumed to be nearly independent of the changes in depletion charge due to deep level emission or capture processes.

If we now recall fig. 3.1 and apply general circuit theory, the transient voltage drop in the insulator can be written as

$$V_i(t) = V_{i,\infty} \cdot (1 - e^{-t/\tau_i}), \quad (3.6)$$

where $\tau_i^{-1} = R_s \cdot C_i$, and R_s can be obtained from the IV characteristics of the device, as shown in chapter 2, whereas $V_{i,\infty}$ can be calculated from Eq. 3.5. The time constant for this expression has been written in terms of emission rate, in order to make it comparable to the term coming from the emission from deep levels (usually noted e_n or p depending on the carrier involved in the process). However, the MIS structure does not fully behave as its equivalent circuit may suggest, since a change in the voltage applied to the semiconductor induces a change in the depletion capacitance that further affects the overall shape of the measured capacitance transient, which will not have a simple exponential behavior anymore, as in a regular junction device.

The charge in the semiconductor, which affects the total measured capacitance,

CHAPTER 3. DEEP LEVEL SPECTROSCOPY IN METAL-INSULATOR-SEMICONDUCTOR DEVICES

Figure 3.3: Simulated transients from the voltage dropped at the depletion region (V_d) and total MIS capacitance (C_T) for the (a) insulator-dominated and (b) the depletion-dominated regimes after applying an external fill pulse from 0 to -1.5 V. White gaussian noise added computationally.

depends not only on the applied bias but also on the total carrier concentration in the depletion region, and on the emission and capture processes following a change in the applied bias, as shown by

$$C_d(n, t) = A \sqrt{\frac{q\epsilon[N_D + n(t)]}{2[V_{bi} + V_d(t)]}}, \quad (3.7)$$

where eq. 1.38 tells us that

$$n(t) = N_T \times e^{-e_n \cdot t} \quad (3.8)$$

is the time-dependent carrier concentration due to emptying the deep levels after the voltage fill pulse.

We can observe in Eq. (3.7) that the capacitance in the depletion region is affected both by the changes in voltage coming from fill pulses $\{V_d(t)\}$, and by the change in carrier concentration in the semiconductor $\{n(t)\}$. This latter processes are the base for the deep level spectroscopy techniques, and imply the existence of thermal or optical excitation of the trapped carriers.

Since the total capacitance that will be measured by the experimental system on an MIS structure is the series combination of the insulator and depletion capacitance (Fig. 3.1), we have to combine Eqs. (3.1), (3.6), (3.7) and (3.8), yielding a general expression for the transient capacitance measured in an MIS diode right after a voltage fill pulse

$$C_{total}(t) = \frac{C_i}{1 + C_i \sqrt{\frac{V_{bi} + V_a \left[1 - \frac{C_{d,\infty}}{C_{d,\infty} + C_i} (1 - e^{-t \cdot e_i}) \right]}{0.5q\epsilon(N_D + N_T e^{-t \cdot e_n})}}}. \quad (3.9)$$

In this equation, depending of the relative relationship between the exponential terms, two regimes can be distinguished:

- Insulator-dominated regime ($e_n \gg e_i$), where the emission from deep levels is faster than the change in voltage, so its small amplitude transient will be undetectable from the overall transient, masked by the larger change due to the voltage effects.
- Depletion-dominated regime ($e_n \ll e_i$). If the emission from deep levels is much slower than the emission from the insulator, the voltage will be able to stabilize

Figure 3.4: (a) Effect of the insulator layer under the insulator-dominated regime and reduction in peak height in the depletion-dominated regime for various C_i/C_d combinations. Spectra obtained from transients with added white gaussian noise. (b) Arrhenius plot extracted for the two traps in (a). The DLTS spectra assumes two traps present at $E_C - 78$ meV and $E_C - 270$ meV with capture cross sections of 2×10^{-18} cm⁻² and 2×10^{-16} cm⁻², and trap concentrations of 2×10^{14} cm⁻³ and 5×10^{14} cm⁻³, respectively. A residual carrier concentration of 1×10^{16} cm⁻³ is assumed.

fast enough for the measurement system to be sensitive to the emission from deep levels, which is smaller in magnitude.

3.2.3 Simulation of DLTS spectra on MIS structures

The two regimes discussed in the previous section, insulator or depletion-dominated, will have different effects on the total MIS capacitance and on the voltage dropped in the depletion region (Fig. 3.3).

In the case of the insulator-dominated transient, we can observe that the capacitance follows the depletion voltage transient, which will be slightly temperature-dependent. This effect will create a nearly flat DLTS spectrum, as shown in Fig. 3.4, with no information about the presence of defects inside the depletion layer.

In the depletion-dominated regime, as indicated in Eq. 3.9 and Fig. 3.4, the amplitude of the simulated change in capacitance is reduced from that which will come from a non-MIS sample. The height of the peaks will be lowered depending on the ratio between the insulator and depletion capacitances. In this regime, the emission from deep levels close to the depletion region edge can be analyzed using the theory found in the DLTS literature [12, 36, 68]. Although voltage and charge values are related, since the changes in the depletion region capacitance after emptying the traps are assumed to be small ($\Delta C_d/C_{d,\infty} \ll 1$), both the insulator and depletion region voltages can be presumed constant. Therefore, the previously analyzed charge process in the insulator capacitor can be neglected, leaving as the dominant processes the charge transients present in the depletion region following an external voltage pulse.

Because of the serial combination of capacitors, the total change in capacitance (ΔC_{total}) of the MIS structure after a fill pulse will be in fact lower than that of a structure without the insulating layer. Using the time dependent capacitance from Eq. 3.9 under the depletion-dominated regime, a general expression for the amplitude of the transient, related with the amplitude of the depletion transient, can be found as

$$\begin{aligned}\Delta C_{total} &= C_{total}(t \rightarrow \infty) - C_{total}(t = 0) \\ &= \frac{C_i^2 \Delta C_d}{(C_i + C_{d,\infty})(C_i + C_{d,\infty} - \Delta C_d)},\end{aligned}\quad (3.10)$$

which can be rewritten as

$$\Delta C_{total} = \frac{C_i^2 \frac{\Delta C_d}{C_{d,\infty}}}{(C_i + C_{d,\infty})\left(\frac{C_i}{C_{d,\infty}} + 1 - \frac{\Delta C_d}{C_{d,\infty}}\right)}.\quad (3.11)$$

Since $\Delta C_d/C_{d,\infty} \ll 1$, then Eq. 3.11 can be simplified as

$$\Delta C_d \approx \alpha \cdot \Delta C_{total} = \Delta C_{total} \cdot \frac{C_{d,\infty}(C_i + C_{d,\infty})\left(\frac{C_i}{C_{d,\infty}} + 1\right)}{C_i^2},\quad (3.12)$$

where alpha (α) is a correctivity factor given by

$$\alpha = \frac{C_{d,\infty}(C_i + C_{d,\infty})\left(\frac{C_i}{C_{d,\infty}} + 1\right)}{C_i^2}.\quad (3.13)$$

Once ΔC_d has been determined from the measured ΔC_{total} , the trap concentration can be obtained from the regular expression used in DLTS/DLOS described in chapter 2, eq. 2.49:

$$N_T = 2N_D \frac{\Delta C_d}{C_{d,\infty}}.$$

The correctivity factor (α) indicates the relative reduction in the DLTS magnitude compared with that of a non-MIS sample. If $\alpha \approx 1$, the measurement will be nearly in perfect match with the spectra coming only from the depletion layer, which is the regime in which ideally the samples should be designed to operate. If this correctivity factor is close to unity, the value for the insulator capacitance does not need to be precisely known in order to have an accurate measurement of the trap concentration. Indeed, the experimental evaluation of this parameter is complicated, since C_i depends on the thickness of the insulating layer, which is difficult to obtain. However, because of the asymptotic definition of α , a low value of C_i will be enough. Besides, the limit on the doping level that can be obtained will be posed by the material becoming degenerate. This is especially valuable in the case of surface treatments in which the final thickness of the obtained insulating layer is quite thin.

When the insulator and depletion capacitance are similar, then $\alpha \neq 1$, and the trap concentration in an MIS diode can easily be derived by knowing the values of C_i and $C_{d,\infty}$. In the case of highly doped samples, or more generally those in which $C_i \approx C_d$, the measured change in capacitance will be lower than that arising purely from the emission from the deep level ($\alpha > 1$). Since the accurate evaluation of both C_i and $C_{d,\infty}$ is affected by a large experimental error, the trap concentrations obtained when $\alpha > 1$ will also show an increased uncertainty in their value. However, although the exact calculation of the trap densities may not be feasible, a good approximation is made possible by the knowledge of the relative magnitude of both capacitances. Simultaneously, the reduction in amplitude sets a limit to the effective sensitivity to trap

Figure 3.5: Correctivity factor for two cases where the insulator capacitance is similar and much larger than the depletion capacitance. Two traps are assumed at E_C -78 meV and E_C -270 meV with capture cross sections of $2 \times 10^{-18} \text{ cm}^{-2}$ and $2 \times 10^{-16} \text{ cm}^{-2}$, and trap concentrations of $2 \times 10^{14} \text{ cm}^{-3}$ and $5 \times 10^{14} \text{ cm}^{-3}$, respectively. A residual carrier concentration of $1 \times 10^{16} \text{ cm}^{-3}$ is assumed.

concentrations. In this case, in order to reduce the effect of noise in the measurement advanced correlation techniques, such as Fourier DLTS [50,150], can be used to analyze the obtained transients.

The simulated DLTS spectra in Fig. 3.4 also shows that independently of the variation of the peak height, the peak temperature positions are not modified. Therefore, the Arrhenius plot obtained in an MIS structure will be the same as that one that would be measured in the absence of the insulating layer (Fig. 3.4b).

Figure 3.5 shows the temperature-dependence of the correctivity factor for two different cases. In the sample where the insulator has a similar capacitance as the depletion layer, the measured DLTS spectra (and therefore the trap concentration) will be lower by a factor larger than four. On the other hand, if C_i is much larger than C_d , the trap concentration obtained from the DLTS measurement will be close to the real concentration of the trap obtained from Eq. 2.49.

Finally, an additional important effect that should be considered from the timing point of view is that during the fill pulse bias the capture rates are usually much faster than the emission rates for a given deep level. This makes the fill pulse behave as being insulator-dominated, increasing the time needed for fully filling the traps by changing the depletion width. Therefore, as a general rule, the fill pulse should be set to be stable after at least three time constants of the insulator ($R_s \cdot C_i$) circuit. Moreover, for fill-pulse dependent measurements (normally used to differentiate types of defects [43]), the correct analysis of the real applied pulse is complicated and will need an accurate knowledge of the capacitances and resistances at different temperatures, which are out of the scope of the present work.

During the fill pulse it is also possible to drive the MIS device into accumulation, with the formation of a majority carrier layer on the surface. These effects will change the transient operation of the device after the fill pulse, and can be useful for the measurement of surface states, something that has been thoroughly described in the literature [104,105,123,147].

Figure 3.6: Device structure for the MIS diodes used during this study.

Figure 3.7: Left: IV curves without insulator and with the insulating layer for the undoped ZnO and the highly doped ZnO:Ga samples. Right: CV curves for the undoped and Ga-doped ZnO layers.

3.3 DLTS analysis on MIS test structures

Once the general expressions have been modeled and simulated for the transient effects in an MIS structure, this section will demonstrate the applicability of this model to MIS test devices measured by DLTS. In order to validate the simulations two homoepitaxial MBE-grown m-ZnO samples were processed: an unintentionally (uid) doped ZnO sample and a highly doped ZnO:Ga sample. The H_2O_2 treatment described in chapter 2 [36, 100] was performed in both samples prior to the deposition of a Au layer, obtaining a thin insulating layer which is needed to achieve high rectification and that was shown to create also an MIS behavior [66, 99, 100] (fig. 3.6). As it can be observed in Fig. 3.7, without the treatment, even for the undoped sample, no rectification is obtained, because of the highly conductive layer that appears on the surface [128] that yields an ohmic contact. In the samples processed after the treatment, rectification is obtained, which indicates modulation of the band bending, and thus the generation of a depletion region that can be used for DLTS measurements. CV profiling yielded a carrier concentration of $\sim 1 \times 10^{16} \text{ cm}^{-3}$ for the undoped sample, whereas the Ga-doped sample shows $\sim 1 \times 10^{18} \text{ cm}^{-3}$. Such high doping makes the realization of rectifying Schottky diodes extremely difficult, and thus DLTS in such highly doped samples is uncommon.

In order to validate the presence of the insulating layer, CV profiles under illumination

Figure 3.8: CV profile under illumination for the undoped sample at 1 kHz. The inset shows the effect of the inversion layer.

were performed at low frequencies (1 kHz), driving the sample into a weak inversion regime, as shown in Fig. 3.8. We can observe that due to the photogenerated carriers the shape of the CV changes from a depletion shape towards a weak inversion profile from an MIS structure on n-type material. This effect has been described in detail before in MgZnO:N films [66]. From the work in refs. [66], [61], and [99] the insulating layer is known to be ~ 10 nm thick since identical H_2O_2 treatments were used on ZnO, which will yield an insulator capacitance of ~ 250 pF. This, combined with the total measured capacitances during the DLTS scans (~ 10 pF, see below), shows that the correctivity factor is $\alpha \approx 1$ for these samples.

DLTS was performed on these films with a 50 ms-long fill pulse at 0 V, and a reverse bias of -1.5 V. The time constant of the sample ($R_s \cdot C_i \approx 10$ ms) is much lower than the 50 ms-long fill pulse time (~ 5 time constants), and thus the traps can be assumed to be totally filled, without significant distortion from the insulating layer. Fig. 3.9 shows the resulting spectrum and Arrhenius plot for the undoped sample, in which three intrinsic bulk traps E2, E3 and E4 are observed. Their trap characteristics including energy, capture cross section, and concentration, are summarized in Table 3.1. The spectrum is dominated by the shallowest trap E2, at $E_C - 100$ meV, and with the highest concentration of all traps, $N_T = 9.3 \times 10^{14} \text{ cm}^{-3}$. Trap E3 is deeper, at $E_C - 300$ meV, and has a slightly lower concentration ($N_T = 4 \times 10^{14} \text{ cm}^{-3}$). Finally, the E4 level shows a trap concentration of $N_T = 2 \times 10^{13} \text{ cm}^{-3}$, over three orders of magnitude below the sample carrier concentration ($N_D = 1 \times 10^{16} \text{ cm}^{-3}$), range which is typically taken as the trap detection limit in double boxcar DLTS. These intrinsic levels have been previously observed by other authors in ZnO grown by different methods, which were summarized in chapter 1, further emphasizing their intrinsic origin, and thus the validity of the measurement in a sample with an insulating layer on the surface, that does not distort the obtained DLTS spectra. Furthermore, because of the correctivity factor being close to unity, no significant reduction in the peak amplitude is produced, and the trap concentration can be directly derived from the DLTS spectrum in Fig. 3.9.

The highly doped ZnO:Ga sample could not be measured by the original double

Figure 3.9: DLTS measurement (RW 2 s⁻¹) for the undoped ZnO sample. $V_r = -1.5$ V, $V_{fill} = 0$ V, $t_{fill} = 50$ ms. The measurement was performed using the double boxcar analysis. Inset: Arrhenius plot showing the three obtained levels.

boxcar DLTS technique due to the low signal-to-noise ratio arising from the high doping level. Thus, Fourier-DLTS was used yielding less noise-affected spectra, as shown in Fig. 3.10. The previously dominant E2 level ($N_T = 9.3 \times 10^{14} \text{ cm}^{-3}$ in the undoped sample) as well as E4 ($N_T = 2 \times 10^{13} \text{ cm}^{-3}$ in the undoped sample) do not appear in the highly doped sample anymore, either because they are not present or below the detection limit.

However, the FDLTS spectrum and Arrhenius plot confirm the presence of the previously observed E3 trap, with nearly the same energy, capture cross section and concentration ($N_T \approx 4 \times 10^{14} \text{ cm}^{-3}$), now over three orders of magnitude below the carrier concentration. Indeed, the comparison of the Arrhenius plot for E3 in both samples (inset of Fig. 3.10) indicates that it is the same trap, whose concentration is unaffected by the presence of Ga, which in combination with results from other authors ([6–8, 97]), further reinforces its intrinsic origin.

Table 3.1: Summary of the obtained deep levels for the ZnO MIS structures by DLTS. Units: Activation energy (E_a): meV; Trap concentration (N_T): cm^{-3} ; Capture cross section (σ_n): cm^{-2} .

	ZnO undoped	ZnO:Ga
E2 ($E_a = 100$)	$N_T = 9.3 \times 10^{14}$ $\sigma_n = 5 \times 10^{-18}$	Not observed
E3 ($E_a = 300$)	$N_T = 3.7 \times 10^{14}$ $\sigma_n = 8 \times 10^{-16}$	$N_T = 4 \times 10^{14}$ $\sigma_n = 6 \times 10^{-16}$
E4 ($E_a = 550$)	$N_T = 2 \times 10^{13}$ $\sigma_n = 2 \times 10^{-16}$	Not observed

Figure 3.10: FDLTS spectra for the highly doped ZnO:Ga sample. $V_r = -1.5 \text{ V}$, $V_{\text{fill}} = 0 \text{ V}$, $t_{\text{fill}} = 50 \text{ ms}$. Inset: Arrhenius plot showing the E3 level for both samples.

Table 3.1 summarizes the results, in which we can observe that the same intrinsic E3 bulk trap is present in both the undoped and highly doped ZnO samples, showing the same trap energy, concentration and capture cross section. Thus, as a result of the insulating layer induced by the H_2O_2 treatment, and despite the large doping level in the ZnO:Ga sample ($N_D \sim 1 \times 10^{18} \text{ cm}^{-3}$), DLTS could be performed on an MIS structure and the trap parameters were fully quantified following the theoretical model developed in section 3.2.

3.4 Conclusions

In this work we have developed and tested a theoretical model to allow the realization of deep level spectroscopy techniques on MIS structures, addressing both the steady state behavior and the transient operation after an electrical fill pulse. The dynamics of the device are highly dependent on the proportion between the insulator and the depletion capacitances, as summarized by the correctivity factor (α) shown in Eq. 3.13. This parameter offers a quick indication of the similarity of the obtained measurement with that coming from a sample in which a Schottky diode was processed without the insulating layer. If the insulator capacitance is large enough (much larger than the depletion capacitance), its exact value does not need to be precisely known in order to get accurate measurements of the trap concentrations. Also, the timing constraints that this layer induce have been analyzed, obtaining two different regimes under which the device can operate when pulsed electrically: insulator-dominated ($e_n \gg e_i$) and depletion-dominated ($e_n \ll e_i$). In the first one, the voltage transient coming from the charge and discharge processes in the insulator dominates the transient operation of the MIS device, masking the transient generated by the carrier emission from the deep levels. Under the depletion-dominated regime, as it has been simulated for DLTS, only a reduction in amplitude is obtained that can be neglected under the right conditions ($\alpha \approx 1$), but the time dependence of the traps is unmodified and so is the Arrhenius plot and the parameters extracted from it: capture cross section and trap energy. Lastly,

CHAPTER 3. DEEP LEVEL SPECTROSCOPY IN METAL-INSULATOR-SEMICONDUCTOR DEVICES

in order to maintain the operation of the device under the depletion mode, the MIS threshold voltage should be considered, especially if measuring at low frequencies, so the device does not shift to the inversion mode.

This theoretical model has been validated with MIS devices processed on two ZnO samples, an undoped one ($N_D \sim 1 \times 10^{16} \text{ cm}^{-3}$) and another one highly doped with Ga ($N_D \sim 1 \times 10^{18} \text{ cm}^{-3}$). By means of a low-frequency CV profile under near-bandgap illumination, the presence of the insulating layer was assessed, and DLTS and FDLTS measurements were performed on both samples. Two intrinsic defects were obtained for the undoped sample, with one of them being observable in the highly doped sample, too. This level, labeled E3 in the literature (chapter 1), shows the same trap energy, concentration and capture cross section in both samples, which is a clear indication of the validity of a DLTS measurement in an MIS device processed in a highly doped sample. The method of creating this insulating layer in order to allow the measurement of such materials has thus proven valuable and can be extended to other materials and/or dopants.

Chapter 4

Development and improvements on the deep level spectroscopic setups

As it was mentioned in the introduction of this document, the thesis has focused not only on the experimental and scientific results, but on the innovation and improvement of the experimental setups and techniques. From a theoretical point of view, the previous chapter described the model developed for the measurement of MIS structures by deep level spectroscopic techniques. However, this could not have been done without a large improvement of the setups used to perform the experiments. Not only the sensitivity of the systems has been enhanced, but also a focus on automation, yield and error prevention has been done. After these improvements, the setups present at the ISOM laboratories are not only able to perform more measurements (in ranges previously unavailable), but do so with much higher signal to noise ratios, and quicker, with more and better organized data available. Additionally, a new fotolithography mask was designed, in order to improve the number of available devices, maximizing the yield and the use of the available material.

4.1 New lithography mask: yield improvements

4.1.1 The old mask

Before 2013, samples were processed using a set of lithography masks that were available at the ISOM laboratories, which allowed for the processing of simple coplanar structures with an extended ohmic contact and semitransparent Schottky diodes. However, this set does not have a lithography step neither for a mesa etching nor a post-Schottky contact addition. This mask was composed of a pattern that included different diode sizes, despite being the $200\text{ }\mu\text{m}$ diameter the only one used for the capacitance studies (because of the good proportion between leakage and capacitance). Fig. 4.1 shows a sample processed using the mentioned mask. The diodes in groups of six correspond to the ones used in the studies, making it directly obvious that a lot of the sample space is lost by making larger and smaller devices. Additionally, as it can be observed, the devices consist only of the extended ohmic plane and the semitransparent Schottky contact. During measurements, the probing tips must be placed with extreme care on the surface trying to avoid any scratch that can easily get through the metal and destroy

Figure 4.1: Example of the old mask diode distribution.

the device. With long measurements, because of any vibration on the table, the tip can move and scratch the device, rendering the measurement unusable and losing a lot of time. Due to the reduced amount of available diodes, some samples have even become completely destroyed without any material left to try a new processing.

4.1.2 Designing a new mask

Considering the limitations posed by the existing lithography process, a new mask was designed. All the needed steps were included in a single 5" mask, simplifying the process and avoiding many small masks that could be easily mistaken. The included steps are as follow:

Alignment marks (optional) If performing mesa etching on transparent materials, such as ZnO, the etched patterns can be difficult to observe and thus align the following steps. Therefore, an initial metalization that only defines the marks needed for the following steps is provided.

Mesa etching (optional) This step is optional, since it can be performed using the ohmic contact lithography. However, if needed, this independent lithography step is provided, considering an extra safeguard distance between the ohmic, mesa and Schottky rings.

Ohmic contact This is the only step which is not optional, since it defines the marks needed during the following steps. However, its main objective is to define the extended ohmic plane, leaving round voids in which to define the devices.

Schottky contact Either this or the next step are also needed, if not both. The Schottky contact allows for the metalization of full circles using whichever metal combination needed. For example, during this thesis it has been common to perform a very thin Au metalization, creating a semitransparent Schottky diode. Several sizes are available, depending on the aim of the study, ranging from $100\text{ }\mu\text{m}$ to $500\text{ }\mu\text{m}$ diameter contacts.

Contact pad Whether alone or in combination with the Schottky contact, a pattern including a ring and a contact pad can be metalized on top of the structure.

Figure 4.2: Example of the $200\ \mu\text{m}$ contact section for a $2.7 \times 2.7\ \text{mm}$ pattern.

For every device size, a concentric design was chosen, aimed for current-injection devices, with the ring(s) diameters chosen so that the injection volume is uniform. For the case of the $200\ \mu\text{m}$ devices, an external ring with a small contact pad is also available. This design is aimed for optical injection, minimizing the shade created by the contact and situating it in the external section of the device, generating the *pacman-style* geometry shown in chapter 2. Also, the pad orientation is changed inside the 3×3 isles that conform the main pattern, so when bonding the contacts do not create shadows. Fig. 4.2 shows an example render of one section containing the $200\ \mu\text{m}$ contact rings.

By using this new design, the number of diodes that could be fitted in a small piece of material largely improved its use, leaving more material left in case of different processing and for new techniques to be applied. Also, since the number of available diodes was increased, many more devices could be characterized, increasing the confidence in the measurements and the safeguards in case any device stops working properly.

4.2 The measurement setup as-found

In order to fully understand the improvements that have been made during this thesis, a first description of the systems present in the lab at the start of this thesis will be performed, mentioning the limitations that existed. It must be mentioned that the basic DLTS system here described was developed by the author as his End of Degree project, and much further developed during the PhD thesis.

4.2.1 Hardware

When this PhD work was started, there was one setup which contained the necessary instrumentation for the measurement of basic electrical parameters, photocurrent, photocapacitance, DLOS and the mentioned DLTS system. A general diagram of the available equipment can be found in fig. 4.3, where the optical and electrical sides have been separated similarly to their physical positions in the setup.

The exact models for the used equipment were:

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

Figure 4.3: Initial setup as found at the start of this thesis.

Digital Storage Oscilloscope (DSO) Two digital storage oscilloscopes with four channels, 1 GS/s acquisition rate and 8 bit resolution were available. Only 2500 samples can be obtained for the chosen time scale, posing an initial limitation to the actual acquisition rate and duration of the obtained waveform.

Waveform generator An arbitrary waveform generator, with 16 bit resolution and high harmonic purity is available. By using the GPIB¹ bus many different waveform and pulses can be configured.

Lock-in amplifier A lock-in amplifier is used. A maximum 100 kHz frequency can be measured with an internal 8 bit digitizer. Its maximum scale is 500 mV and minimum 1 nV, which allows for a high dynamic range. A current input with a gain of 10^6 V/A is available, although its noise levels do not allow for the use of the smaller scales. A voltage input is also available.

Voltage source A KeithleyTM model 230 voltage source is used to generate the necessary excitation during photocurrent and IV profiling. It can be controlled easily through the GPIB bus with very little configuration being necessary.

Current meter A multimeter is used as a pico-ammeter. It can measure currents down to femtoamperes, with an automatic scale configuration and GPIB control.

Capacitance meter The BoontonTM model 7200² capacitance meter has been used for the photocapacitance and DLTS measurements at 1 MHz. This meter allows for

¹General Purpose Interface Bus, or IEEE-488, created by Hewlett-Packard during the 1960s. It is widely used in instrumentation environments, although lately its use is being substituted by faster communication protocols such as USB.

²Sadly, BoontonTM does not manufacture this equipment anymore.

4.2. THE MEASUREMENT SETUP AS-FOUND

the addition of a bias to the AC probing signal, which can be injected from an external source. Additionally, an analog signal proportional to the capacitance and loss values can be obtained from the rear panel, which can then be digitized using the DSOs.

UV lamp A 1000 W Xe lamp is used for the UV measurements, with a water filter attached to eliminate the excess of IR light. A quartz lamp is also available for IR measurements, although it has not been used during this thesis.

Monochromator A 1/4 m monochromator, with three variable gratings and six filters has been used to select the wavelength of the illumination on the sample. The grating and filter change is automatized and controlled from the computer through the GPIB interface. The monochromator also includes a shutter that can be controller by software or using a TTL signal through a BNC connector.

Fast shutter Since the internal shutter present in the monochromator has a transition time that can be too long for optical transients to be detected, a fast shutter can be added to the optical path. It is controlled using a TTL signal provided from any 5 V configurable source. Initially, this was performed through one of the analog outputs from the lock-in amplifier.

As it can be observed from the many equipment available, each technique will require the connection of different instruments in a certain configuration. In this initial setup, for capacitance-based measurements (DLOS, DLTS and CV), only fixed scales could be used, which had to be manually configured by the operator during the initial setup. Therefore, a previous knowledge of the samples needed to be available, and many measurements were discarded either because of a large signal-to-noise ratio (SNR), saturation of the measurement, or even both.

4.2.2 Software

Many different programs and routines³ were found in the setup, which could perform all the available techniques: IV, CV, photocurrent and DLOS, as well as photocurrent in transient operation.

Each program was named after the technique and the equipment used, existing a different virtual instrument (VI) for each combination of instruments (for example, there existed a different CV program for the measurement at 1 MHz and another one for lower frequencies using the lock-in amplifier). Although this issue has been maintained in the latest versions, it has been reduced substantially. Moreover, the initial routines were lightly nested, with many duplicities between programs repeating code. No error cluster routing was used nor error-dependent execution was implemented, reducing the long-term stability of the software. It was not uncommon for a VI to halt execution without an indication of the error source. As for the internal organization of VIs, they relied heavily on stacked and flat sequences, instead of fully embracing the data flow paradigm recommended by National InstrumentsTM for LabVIEW programming.

³During the present section, *program* will refer to fully functional pieces of software that accomplish the totality of a measurement, i.e. an IV profile. Routine will be used to point to parts of one of those programs which generally can be called from multiple places. However, some of these routines can be called independently, i.e. the one that initializes an instrument.

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

Moreover, the *version control* of the software consisted on a complete copy of the folder that contained the software, with an increment in the version number. No LabVIEW project nor libraries were implemented, making the dependency checks practically impossible.

4.2.3 Main limitations

The principal issues and limitations found in the system as found were:

Software organization Because of the light nesting and the lack of libraries or a LabVIEW project, fixes in one VI could not be easily propagated. Additionally, if a routine was modified affecting other VIs, this issue could not be detected and thus corrected. The structure of the block diagrams made it difficult to understanding, enhance and modify the programs and routines.

Sensitivity: Scales and centering Since there existed no centering nor automatic scaling on any of the capacitance-based systems, the full-scale resolution could not be adapted to the actual magnitude of the measured signal, thus losing sensitivity. Therefore, CV profiles were sometimes very noisy since they had to be measured using large scales. Transients for DLTS were difficult to obtain for the same reasons.

Sensitivity: Data acquisition The lock-in amplifier, capacitance meter and DSOs have internal 8-bit digitizers which were used for the acquisition of the measured values. This limits the effective voltage resolution and reduces the SNR of the measurements.

Sensitivity: Timing Since the samples from the lock-in and the capacitance meter were obtained through the GPIB interface, which is not designed for speed, the number of samples per second (S/s) that could be obtained was pretty low, in the order of $10 - 20 S/s$, thus limiting the shortest transient effect that could be measured from these equipment. Also, for steady-state values, oversampling and averaging is a common practice to reduce noise and increase the confidence in the obtained values. Due to timing constraints, the number of samples acquired for each step was kept low. Lastly, the DSOs only provide 2500 samples for the configured time base, thus limiting the timing resolution of the system. Both for DLTS and DLTS the chosen approach was to use two DSOs, each one with a different time base, to obtain a long and a short transient. However, oversampling and filtering is complicated with such a small number of available samples.

4.3 Hardware improvements

This section will describe the improvements carried out in the hardware side of the setup, which comprises the design of a new amplifier for low frequency capacitance measurements, the implementation of an advanced centering device in the 1 MHz capacitance measurements, the addition of a new digital acquisition (DAQ) system for improved sensitivity, and the design of a remote control box to operate the shutters, lamps and monitor the water filter temperature.

Figure 4.4: Schematic for the transimpedance amplifier designed for the low-frequency capacitance measurements.

4.3.1 Frequency-dependent measurements: low noise transimpedance amplifier

As it was mentioned in the previous sections, in the initial setup the low-frequency capacitance measurements were carried out using the SR530 lock-in amplifier. In chapter 2 it was described how for measuring the capacitance from a diode, its AC current is measured upon the excitation with an AC+DC voltage. However, for the sake of the measurement itself, that current is first converted onto a voltage value that is then demodulated using the lock-in instrument.

The SR530 model provides a current input, although with a fixed gain of 10^6 V/A and a noise level of $0.13 \mu\text{V}/\sqrt{\text{Hz}}$ at 1 kHz, which is the expected value coming from thermal noise for the internal transimpedance amplifier feedback loop. This gain proved to be far from optimal for some of the measurements carried out in the study presented in chapter 7, where because of the MIS accumulation layer close to the bandgap, the capacitance values largely rose, consistently saturating the current input of the lock-in amplifier. However, for measurements at lower frequencies and without illumination, the noise levels were too high for the measurement to be reliable, and the signal level too low.

Therefore, a decision to design a custom current-voltage (technically, transimpedance [31, 124]) amplifier was taken. A two-stage design was chosen, in order to allow for greater gains to be achieved without compromising stability. Fig. 4.4 shows the schematic for the final design, in which it can be observed that the first stage has a fixed gain of 10^4 V/A , whereas the second stage is configurable. This first stage has been implemented using the OPA140 transimpedance from Texas InstrumentsTM, which is a high-precision Operational Amplifier (OA), with a noise level as low as $5.1 \text{ nV}/\sqrt{\text{Hz}}$. However, although better voltage noise levels can be attained using other amplifiers, the low current drift and low input current values make it ideal as a first stage for this application. Indeed, any change in the input current will change the bias point of the device under test, which will distort the experiments. Moreover, the OPA140 ultra-low current noise value makes current noise negligible, which is ideal for high impedance sources, as is the case with reverse-biased junctions. The capacitor added to the feedback loop configures a low-pass filter with a cutoff frequency of $f_c = 159 \text{ kHz}$, which filters the excess noise outside the measurable spectra, limited by the lock-in amplifier at 100 kHz.

The second stage is a simple inverting amplifier, with a gain configured by changing the resistor placed in the feedback loop. A resistor with a low value of only 10Ω is placed between the two stages, in order to reduce thermal noise, which is proportional to the

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

resistor value (around $0.4 \text{ nV}/\sqrt{\text{Hz}}$)⁴. The PCB has two available ports in the feedback loop, with which to configure the desired gain/attenuation, plus the cutoff frequency of the second stage. This proves valuable if measuring at low frequencies, where the whole 100 kHz range is not needed and can be filtered out to reduce saturation on the lock-in amplifier. The chosen operational amplifier was the AD797 from Analog DevicesTM, an ultralow noise (only $0.9 \text{ nV}/\sqrt{\text{Hz}}$ at 1 kHz -typical value-), ultralow distortion with excellent AC characteristics. Since this second stage is usually configured with low gain values, the amplification performed on the noise coming from the first source is small. With the noise added by the second stage being also low, the total noise contribution from the transimpedance amplifier can be kept at a reasonable value.

With this custom-made transimpedance amplifier, some samples could be measured with larger gains than the fixed one offered by the existing equipment, whereas others could be configured for lower values, being able to observe large capacitance changes which tended to saturate the current input in the lock-in amplifier. Additionally, since both stages are designed using low noise components, the overall noise behavior of the amplifier allows for high quality measurements to be carried out.

4.3.2 Advanced centering

During capacitance measurements (DLOS and DLTS mainly), the steady state values can change largely with temperature or illumination energy. Also, the measurement equipment have limited number of available scales, so maintaining the transient signal centered in any of these scales, in order to maximize the sensitivity, can be difficult. This section will focus on the 1 MHz measurements using the Boonton 7200 capacitance meter. For the case of the lock-in amplifier, the centering is performed using the internal configuration from a purely software-based point of view.

Prior to this thesis, a fixed capacitor could be added to the centering port in the capacitance meter in order to offset the measured value and try to reduce the scale, thus maximizing the dynamic range when digitizing. However, this approach was only good for small changes in the controlled parameter (temperature or illumination energy), since for any large change in the background capacitance, a re-centering would be needed.

Subsequently, a dynamic centering was needed for the 1 MHz capacitance measurements, which could be controlled programatically, in a similar way to what can be done in the lock-in amplifier based scans. For doing so, a capacitance offset box, specifically designed for the Boonton 7200 instrument was acquired from Dr. Aaron Arehart, which using simple LabVIEW commands, can offset the capacitance measurements in 0.125 pF steps. This basically allows to use the smaller scales throughout the whole scans as far as the conductance limits are not overpassed.

4.3.3 Improvement on acquisition rate: oversampling and filtering

In the previous section the issue with centering was tackled, but optimizing sensitivity just on the analog signals does not really enhance the system as long as the digitization is performed using low resolution equipment. The DSOs approach proved inefficient, since the theoretical limit in their resolution could never be reached in practice because

⁴However, this low resistor poses a large stress on the first stage. Because of the large negative feedback gain of the OPA140, stability is granted, although a higher value could help reduce the effect of fluctuations and drifts in the amplifier parameters.

Figure 4.5: Example of a low-amplitude transient with noise and the effect of a moving average filtering.

of the difficulties stabilizing the signals. Ideally, using the minimum 2 mV scale, the smallest voltage step that could be resolved would be:

$$V_{min} = \frac{2 \text{ mV/div} \times 10 \text{ div}}{2^{28} \text{ bits}} = \frac{20 \text{ mV}}{256} = 78 \mu\text{V} \quad (4.1)$$

Also, the timing for the transient capture was being compromised, since the DSOs only provide 2500 data points for the given time scale. With the old DLTS system, the shortest transient being captured was 50 ms-long, which allowed to measure RWs as high as 1000 s^{-1} . Therefore, the minimum time resolution or effective sampling rate would be:

$$t_{min} = \frac{50 \text{ ms}}{2500 \text{ S}} = 20 \mu\text{s} \quad (4.2)$$

$$f_{max} = t_{min}^{-1} = 50 \text{ kS/s} \quad (4.3)$$

With such low number of data points and sampling rate, any advanced signal processing technique could not be implemented, thus limiting the resolution of the whole system. In order to increase both the acquisition rate and vertical resolution, an advanced DAQ solution was acquired from National InstrumentsTM. It consisted on a PCIe board with a noise rejecting connector block. It provides 16 analog input with 1.25 MS/s at 16-bit resolution. The full-scale voltage can be configured for many ranges. However, since the Boonton 7200 instrument outputs are 2 V full range, when choosing the $\pm 2 \text{ V}$ range, a voltage resolution of $61 \mu\text{V}$ can be obtained, without the need of constantly changing the scale. This value is lower than the one obtained for the best scenario using DSOs. Also, the increased sampling rate allows for advanced filtering and signal processing techniques.

In the final implementation, a 1 MS/s acquisition rate was chosen, which allows for the detection of very fast transients, pushing the maximum RW in the DLTS system

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

up to 8000 s^{-1} . Since the noise levels coming from the system are usually high, the acquired transients can be filtered, since the sampling rate is much larger than the maximum representative frequency.

An easy to perform filtering option is a moving average, which directly smooths the data. More technically, a moving average is a low-pass filter very effective reducing random noise while preserving sharp responses in the time domain, especially if the acquisition rate is large enough [103]. Additionally, if using multi point moving average implementation (such as Henderson or Spencer methods), every data point in the output data will have information about the surrounding points (fig. 4.5). Therefore, when decimating the data array to reduce the memory occupation (for example, when saving to a file), the amount of lost information is minimized. A similar approach was applied for capturing capacitance values from the lock-in amplifier, only widening the dynamic resolution from the DAQ board to follow the $\pm 10\text{ V}$ signals coming out from the SR530 instrument.

But the addition of this advanced DAQ solution did not only enhance the transient capture resolution, but also the steady-state measurement of capacitance values. As it was mentioned earlier, both the lock-in amplifier and the capacitance meter have internal digitizers, with 8-bit resolutions, which can be obtained through the GPIB bus. This process does not only suffer from the reduced resolution, but is slow, making the acquisition of a large number of samples to be averaged a time-consuming task. Therefore, measurements had to be either slow or noisy. However, by applying the new DAQ board, a rocketing number of samples are acquired in very few time, which can be averaged to reduce the effect of white noise. Not only the number of samples is larger, they are also acquired with a larger resolution, minimizing the quantization error noise.

4.3.4 Automatic lamp control & water filter temperature monitoring

An issue arising from the long persistent photo-effects shown by some samples was that they needed to be left resting for long hours before the measurements could start. However, this start time could be far from the opening hours of the lab. Additionally, the finishing time of a scan could happen before the opening, leaving the equipment on for a long time. The most sensitive instrument that suffers from long hours turned on is obviously the UV lamp, which uses up a great deal of power, too.

With the help of the final degree project student A. Gómez, a box for controlling remotely the UV lamp was developed. It includes the necessary isolation and power electronics needed to safely turn on or off the high-power source with simple instructions from the computer. Additionally, it provides digital output signals to control both shutters (the monochromator internal one, and the external fast shutter), leaving the signal generator free to be used in any other measurement it may be needed.

Another issue that was detected during the long operation of the system was the excessive heating and even the clogging of the recirculating water which helps maintain it cold enough for the water not to boil. The designed control board also includes a port for plugging in a K-type thermocouple that can be attached to the water filter and monitor it for excessive temperature. This allows the system to turn off the lamp if a certain threshold is reached.

4.4 Software improvements

Besides the hardware improvements described in the previous paragraphs, the other big effort has been placed on software and automation improvements. The user interfaces (UI) have been updated to take advantage of bigger screens, and be more focused on the results, grouping configuration parameters. Internally, the VIs have been cleaned and divided into easier to maintain pieces. These improvements will be described during the following sections.

4.4.1 Capacitance values

In the existing programs that used the lock-in amplifier, even though the current input gain was constant, a conversion factor had to be manually included through the front panel, in order to obtain capacitance and conductance values. These values were noted in a text file, although they could be calculated analytically from the simple impedance measurements theory presented in chapter 2. Therefore, the front panel was simplified, with the operator having only to provide the amplifier gain and frequency, with the software calculating all the needed conversion factors.

As it was mentioned in the previous section, centering and autoscaling were implemented for the lock-in amplifier measurements. A complex routine was developed for centering the signals and choosing the optimal scale from among the many offered by the equipment. Since the internal centering capabilities are limited to one full scale value, the centering process stopped when any of two conditions applied: no further centering could be configured or the signal went out of scale. This proved extremely useful for the measurement of small signals and to resolve the CV shape of depleted samples.

Another improvement was the addition of the measurement of both conductance (losses) and quality factor values, either at 1 MHz or low-frequency systems. Since the capacitance values are affected by the offset point (whether it is hardware or software configured), the Q-factor had to be analytically computed from the offset-corrected capacitance value and conductance measurements.

4.4.2 Timing

One of the issues with DLOS/DLTS measurements, which also affects other techniques, are timing constraints, since each measurement step is carried out dozens of times, a single second improvement for each step can lead to large gains in overall measurement time. During the years that this thesis has lasted, several minor improvements in the measurement timing have been implemented, revising all the crucial steps that were repeated in order to minimize the scan time. By doing so, in combination with the added capabilities, some scans have been reduced even to a third of their previous duration.

A timing estimation routine was developed, which by taking the history of step duration and target parameter variation, dynamically calculates the estimated time of end for the current measurement, which can be fed to the UI and shown to the operator. This has helped also detect inefficiencies in the step routines, allowing for further improvements on the system.

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

4.4.3 Data saving

In the old system implementation, each program had its own routine for saving the resulting data. This was not only inefficient, but complicated. Therefore, the objective was to create a single and understandable file format for the data gathered from different techniques. Generally speaking, a measurement will have a header indicating the sample name, measurement parameters, etc. Then, as many columns as measured parameters are added to the file. Each column should indicate the name of the parameter and the units in which the values are represented. This simplifies the import of data into software such as Origin©, Matlab©, etc.

A routine was developed to carry out all these functions. This sub-VI allows to initialize a file with the header and column designators (name and units), and then add the rows one by one during the measurement. This way, if a power outage or any other system failure occurs, the already measured values will be already saved to disk. This was not the way chosen in the former implementation, where all the data was saved at once at the end of the scans, meaning that any error could lead to data being lost.

4.4.4 Custom optical changes

During DLOS and photocurrent measurements, sometimes a feature in the spectra happened at an energy coincident with a filter or grating change. Since many of the filters could be used in energy ranges which are not the automatically-configured ones, an option to provide a custom set of filter and grating changes was implemented. By doing so, the coincidence of these changes could be avoided.

4.4.5 Many-RW measurement

In the initial DLTS implementation, only four RWs at a time could be acquired, because of the limits in the acquisition system, based on DSOs. After the implementation of the advanced DAQ board, there was no limit to the minimum and maximum duration of the transients. Therefore, from the fixed RW sets the configuration was changed to a flexible array-based option. The operator can select any RW, with any beta parameter to be obtained, with the system acquiring the transients of the necessary duration automatically.

Moreover, since the fastest transients (higher RW) are more affected by noise, they usually need more averaging. The system allows to configure different number of repetitions for each RW, in order to equilibrate the SNR for each transient duration. Indeed, since the calculation points in double-boxcar DLTS are sometimes concurrent, any transient can be useful to compose an aggregated transient with the addition of all the measured transients, regardless of their duration. A routine to perform this task was developed, which aligns, filters, resamples and aggregates transients dynamically at each DLTS step, creating a full transient that can then be saved to disk and used for any calculation method.

4.4.6 Fourier DLTS

In chapter 2 the details of the FDLTS technique were described, but their implementation poses some issues. First, the concept of Rate Window does not apply, with the only parameter defining the transient emission rates is the transient duration. Therefore, a first implementation was made around this idea, capturing a single transient at

each temperature and calculating the time constants as shown in the theory. However, although each scan was intrinsically faster, since less averaging and shorter step timing could be used, the optimal transient time was very difficult to achieve.

Yet, during DB-DLTS scans, many transients at radically different lengths were already being recorded. Subsequently, by performing Fourier analysis on the transients with lengths needed for each of the rate windows, many target emission rates were being observed. Not only increases this the number of available data points, it is basically *free* in terms of the scan duration. This advanced signal analysis, albeit being expensive computationally, can be done in parallel, taking advantage of the intrinsic multitasking capabilities provided by LabVIEW.

Indeed, the final implementation uses the aggregated transient described in the previous paragraphs, and obtains the emission rates at different lengths by slicing it. This allows for the process to occur while the system is already measuring the next step, using a noise-reduced transient with information from many shots, without rising the memory footprint beyond the computer limits. Additionally, the transient amplitude is obtained for each of the valid data points, which can be easily translated onto defect concentration, which is recorded along with all the previously mentioned parameters.

4.4.7 Transient saving

Depending on the slowest RW (longest transient duration), each transient can contain millions of data points, which occupy a great amount of memory and disk space. Although storage is getting cheaper with time, it is still a valuable asset to be considered in any software system. Therefore, an effort was placed on making the saving of transients as efficient as possible. Firstly, the file format was changed from text-based (ASCII) files to binary formats, which store more efficiently large amounts of data, despite this files not being directly readable using notepad-like viewers.

A routine for saving the transients was implemented, which from the original aggregated transient, generated a filtered and decimated version, smaller in memory footprint. This reduced transient is then saved to a temporary file which is added to a zip folder, applying compression methods to further reduce the storage occupation. However, after a whole DLTS scan, several hundred megabytes can be used. Thus, saving the transients has been made optional through the DLTS program front panel.

4.4.8 Data analysis

Gathering large amounts of data is not useful if no powerful analysis tools are available. Concurrently with the development of the measurement techniques, these analysis tools have been developed. From basic electrical characterization to complex Fourier-DLTS scans, a program has been added to the project.

IV analysis

As it was described in chapter 2, from the simple IV profiles a lot of information can be obtained, such as the Schottky barrier height, ideality factor, and series and contact resistances. Previously, this process had to be performed by hand, with the help of the fitting capabilities of other software. However, this resulted in a tedious process if many measurements for different samples and devices had to be analyzed. A program which loaded the IV curve and helped analyze it was developed. By providing simple

Figure 4.6: Example IV with the linear and flat regions highlighted.

information such as the diode area, and graphically choosing the linear region and the series-resistance affected one, all the previously mentioned parameters were given by the software, largely improving the analysis throughput.

As an example, fig. 4.6 shows a device IV curve in the forward bias region, with the linear and flat parts of the spectra marked, along with the parameters that can be obtained from them. In the software, these regions are selected using cursors, showing the fitting curve, for the operator to check the validity of the selection.

CV + Doping profile

From the CV scans a doping vs depth profile is obtained, depending on the materials dielectric constant and the device geometry. Previously, in order to obtain this doping profile, each CV measurement had to be analyzed individually upon completion of the scan. However, there is no practical need to wait until the end, and the analysis is computationally easy. Therefore, it was included in the measurement programs, showing the doping and depletion depth values dynamically during the scans. These computed values are saved along with the capacitance, losses and Q-factor values in a single file at the end of the scan. In case further analysis is needed, or any of the calculation parameters need be changed, the standalone analysis tool is still available, adapted to the new file format.

DB- and F-DLTS

DLTS measurements generate a large amount of data in the final implementation. Each scan can measure up to 14 rate windows, both by double-boxcar and Fourier analysis, along with the transients for each step (this is optional) and capacitance-temperature (CT) profiles. Moreover, neither of these datasets provides direct information about the signature of deep levels, being necessary the intervention of a human operator.

In order to simplify the task of analyzing the DLTS scans, two software pieces, one for double boxcar and another one for Fourier DLTS were developed. The basic idea common to both implementations is the processing of either of the measured datasets, and generation of an Arrhenius plot along with the defect signature (activation energy, concentration and capture cross section), with their corresponding dispersion statistics.

For the case of the DB-DLTS scans, the program provides a user interface which after loading the measured ΔC values for each RW, adds a cursor with which to manually position the maximum in the DLTS spectra. Each RW can be shown individually, or aggregated, and any change on the cursor position automatically updates the Arrhenius plot and the computed values. In order to help the operator, the spectra can be filtered using any of the methods provided by the LabVIEW libraries. Additionally, in order to compensate the effect of the equipment relaxation in the shorter rate windows, which create an apparently negative ΔC value, the measurements can be de-baselined. For doing so, the implemented routine obtains the minimums (valleys) in the RW spectra and calculates an equivalent baseline which can be subtracted, *flattening* and equalizing all the RWs. All these helping functions are optional, and it is up to the operator to decide and check the validity of the final result, specially in very noisy measurements where the calculations can lead to unrealistic results.

DLOS transients

As it was explained in chapter 2, the DLOS technique originally described by Chantre *et al* [16] defines two main parameters obtained from the photocapacitance scans. The steady-state value is easy to obtain and analyze, since the onsets give direct trap energy positions and the height of these onsets are easily translated onto concentrations. However, the optical cross sections, obtained from the derivative at $t = 0$ from the capacitance transients, are difficult to compute, since the measured transients are sometimes affected by noise, persistent photo-effects, etc.

Therefore, an analysis program was developed to assist the researcher during this operation. It allows to load the steady state value, along with the transients captured during the scan. By a combination of filtering, zooming, and cursors, it allows to define a region of the transient in which to calculate the derivative and obtain the cross section. Additionally, by employing an exponential fit, a less noise-affected version of the steady state, computed from the infinite value from this fit can be plotted, helping to the identification of small onsets. However, during this thesis, all of the shown spectra have been directly plotted from the in-measurement steady state values.

4.4.9 General software optimization and modernization

Additionally to the many improvements described in the previous sections in this chapter, most of them applicable to some equipment or measurement technique, some general improvements have been propagated along all the software collection that has been used during this thesis.

Code organization: version control and project management

As it was mentioned earlier, all the VIs that composed the measurement suite were organized inside a folder in the computer, with the only version control system in place consisting on a number added to this folder. The sub-VIs were found in the same hierarchy, which sometimes complicated finding the main programs. But the most important improvement was to add all the existing routines to a LabVIEW project, from which the software could be easily managed. This allowed to detect duplicities (same VI used from two different disk locations), broken dependencies, etc. Moreover, it helps clarify the organization of the software onto programs and routines, by creating virtual folders into which sub-VIs are placed.

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

Additionally, in order to synchronize the folder between different computers, maintain a single version and track the modifications, a git repository was configured. By doing so, each modification could be added to the log with a message, and parallel development branches could be used, maintaining at least one stable and one development tracks, so general users did not suffer temporary inconsistencies in the development versions.

UI improvements

As a general rule, the user interfaces were given a cleaner look-out, grouping related parameters in clusters, which at the same time simplified the block diagram. All these clusters were given Type Definitions, so regardless of the hierarchy level they were used on, they maintained the same data structure. This avoided excessive type casting, as recommended by National Instruments.

Additionally, both graphs and configuration parameters were grouped at a higher level using the tab control, so the operator is allowed to navigate through related configurations without having to find them among many controls in the front panel. Similarly, for programs that return large amounts of data such as the DLTS one, indicators are tabbed, so each graph can be accessed individually and in a bigger format. Also, some important buttons such as the start and stop ones have been increased in size, to help pushing them when acting through remote connections, where screens are sometimes downsized (for example, accessing with a smartphone). Moreover, some of the graphs are dynamically configured at run-time, in order to respond to the parameters introduced by the operator (for example, in the DLTS program, the label for the RWs is changed depending on the ones configured, disabling all unnecessary plots).

Internal architecture

However invisible from the outside, the overall structure of almost all of the main programs, plus the sub-VIs, has been reworked to modernize, simplify and divide their operation. From a flat, unorganized block diagram, the big programs have been moved to state machine structures, simplifying the debugging and maintenance of the software pieces. The excessive use of internal variables, flat or stacked sequences, etc, has been avoided. Therefore, the overall readability of the code has been largely improved, with debugging and scalability made also easier.

As an example, fig. 4.7 shows a very basic generic state machine, with the different states configured in a type definition enum, so the number of states can be easily increased or reduced by changing code from a single file.

Stability: error cluster management

In the old version, the error cluster was usually kept unconnected inside the block diagrams. This made the routines to stop at any error randomly at any point in code. This does not only break the data flow paradigm, but prevents the shutdown of the systems in a proper fashion. Code pieces that depended on previous data were executed regardless of the validity of that data.

In order to avoid this issues, the error cluster has been connected throughout the whole project, ensuring the correct execution order without the need for structures. Additionally, all of the new routines, plus the old ones that have been refurbished, now perform an error check prior to any execution, returning without further operation if the input error cluster shows a previous failure.

Figure 4.7: Example of a state machine with runtime error detection and handling.

For the main programs, error checking at each iteration has been added, executing an error step before exiting the program. This allows to disconnect any signal and save any pending data may any error happen randomly during execution. Fig. 4.7 shows how this is handled in a state machine in which upon detection of an error, the error state is executed and the program shut down.

Security

In the setups, a multiuser environment has been configured, with each user/group having their own desktop and limited privileges. Previously, measurement data was stored in a public folder, where anyone could access it, both from the network or from any user. This does not help maintain data secret where needed. Also, any user could modify the software.

In order to solve this situation, most of the users have limited access rights, being allowed to only write data to their private folders. Also, the code does not save from those users, being necessary to have administrator permission to modify the software. This allows to preserve the overall consistency and traceability of the measurement systems. Moreover, in case the code is accessed and copied to another computer, it is password-protected, which helps to avoid unintended users to make any modification, even in computers outside the control of the laboratory.

4.5 The aftermath

Fig. 4.8 shows the final collection of instruments with which the laboratory is now equipped. In yellow the newly designed or added equipment can be observed. It is worth mentioning the elimination of the DSOs, which place no role in the final implementation. For DLTS measurements a cryostat and temperature controller are also available, although they have been not shown in the figure.

Overall, after many years of continuous work on the characterization systems, the measurement setups have been placed a step further in their capabilities, by a combination of hardware design and implementation, and software development. The improved

CHAPTER 4. DEVELOPMENT AND IMPROVEMENTS ON THE DEEP LEVEL SPECTROSCOPIC SETUPS

Figure 4.8: Schematic of the final setup, highlighting the newly included equipment.

sensitivity has allowed to detect deep levels with lower concentrations than were previously observable, in a fraction of the time needed before.

Part III

Experimental results

Chapter 5

Deep level analysis of homoepitaxial ZnO in non-polar and semipolar orientations

Presented at the 9th International Workshop on Zinc Oxide and Related Materials, celebrated in Taipei, Taiwan between October 30 and November 2, 2016.

5.1 Introduction

Chapter 1 thoroughly introduced the main issue that arises with ZnO, which is the lack of reliable p-type doping, coming partly from a large intrinsic n-type behavior. Many dopants have been proposed to achieve this desired conductivity, and some efforts on N-doping will be presented later on this thesis. Additionally, the source of the intrinsic n-type, with usually large carrier concentrations, remains unclear. It is not unusual for the ZnO samples, undoped, to show electron concentrations in the range of $10^{16} - 10^{17} \text{ cm}^{-3}$, although lower residual carrier concentrations have been attained.

High quality growth techniques, among which MBE shows the best results, are crucial to understanding the origin of this consistent n-type behavior. The availability of good quality substrates from well-renowned manufacturers such as Crystec and Tokyo Denpa¹ allowed to investigate homoepitaxial films, trying to reduce the amount of defects and strain coming from heteroepitaxy. Chauveau *et al* showed that homoepitaxy in non-polar orientations allows for the carrier concentration to be reduced to values as low as 10^{14} cm^{-3} [17, 135]. Among the various crystalline orientations in which ZnO can be grown, m-plane has shown the best results.

However, the first question that needs to be answered is whether this reduction in carrier concentration comes from a reduced number of intrinsic donors (or generally, donor-like defects), or by compensation from other acceptor-like defects (such as the V_{Zn}). Growing the best material quality will be of the utmost importance for the obtention of p-type conductivity. In this study, the best results were obtained for the m-plane orientation, which will be used as a baseline for the N-doping study presented in chapter 6.

¹Unfortunately, Tokyo Denpa does not provide ZnO substrates any longer.

Figure 5.1: Structure for the devices used in this study.

Figure 5.2: IV profiles (left) and carrier concentration profiles (right) for the three samples.

5.1.1 Samples description

A complete analysis of the defects present both close to the CB and to the VB will be presented for three samples grown homoepitaxially by MBE at CRHEA-CNRS in France by the group led by Dr. Chauveau. They were grown in the non-polar a- and m-orientations and the semipolar r-plane, on the best quality substrates available, provided by Tokyo Denpa. Previous results show that under these conditions, the material quality, measured by structural techniques is indeed high [18,19]. The samples thicknesses were chosen large enough ($1.5 \mu\text{m}$) so that the depletion region of the finished devices lays entirely in the epilayer, as shown in fig. 5.1.

5.1.2 Electrical characterization of the devices

Schottky diodes were processed as referred in chapter 2 (fig. 5.1). Basic electrical characterization consisted on IV and CV profiling of the samples to assess the electrical quality of the processed devices (fig. 5.2). The IV profiles show very good rectification properties for all three orientations, with r-plane having the largest direct-to-inverse rectification ratios, probably because of processing inhomogeneities.

For the case of the CV profiles, the obtained values for the carrier concentration indicate that the m-plane sample is the one with the lowest net doping, of $\sim 2 \times 10^{16} \text{ cm}^{-3}$. On the other hand, both a-plane and r-plane, despite being different in polarity, show the same value of $6 - 10 \times 10^{16} \text{ cm}^{-3}$, nearly four times larger than the m-plane sample. All these values were obtained in the dark at 1 MHz, with all devices having good quality factors for the capacitance measurements.

5.2. OPTICAL DIFFERENCES BETWEEN NON-POLAR AND SEMIPOLAR ZNO

Figure 5.3: PL spectra for the three grown orientations both at room temperature (left) and low temperature (right). Vertically shifted for clarity.

5.2 Optical differences between non-polar and semipolar ZnO

In order to assess the crystalline quality of the material, as well as the optical signatures of both donors and acceptors, continuous-wave photoluminescence² was measured using a He-Cd laser (325 nm wavelength) both at low temperature (8 K) and room temperature, as shown in fig. 5.3.

Room temperature PL

At room temperature (RT) the samples look more alike (fig. 5.3-left). Both r- and a- planes show a larger defect band, which possibly correlates with their also larger net carrier concentration measured by CV (fig. 5.2). However, the energy positions of all the observed features are similar between the non-polar orientations. Their defect band is centered around 2.45 eV, whereas for the r-plane sample its center position is lower in energy, around 2.3 eV. Also, the PL relative intensity is lower for the semipolar orientation.

When observing the near-bandgap emission (NBE), it is clearly observed that for the non-polar samples it is centered in a donor-bound exciton (D^0, X) emission around 3.283 eV. Taking into account the exciton binding energy and the RT bandgap, this emission yields a donor energy position of about 25 meV. Interestingly, this value correlates with a defect that could be observed by DLTS, as will be described in a following section. For the r-plane sample, the NBE emission is centered higher in energy, without reaching the free exciton (FX) at an energy around 3.301 eV. Therefore, it might be related to a different donor, possibly a reduced presence of the shallower donor found in the non-polar samples. The defect responsible for this emission is shallower in energy, explaining why it has not been observed by DLTS.

Low temperature PL

As for the LT-PL spectra (fig. 5.3-right), the similarities in the defect band between the non-polar samples disappear, with the m-plane layer having the emission centered

²Special thanks must be placed in this section to the hard work from Víctor Jesús Gómez Hernández, who helped measure and re-measure all samples in order to ensure the correct assignment for all samples.

Figure 5.4: Left: Near bandgap emission for the unintentionally doped samples for the three orientations, with tentative assignments to the observed peaks and their replicas.

around 2.2 eV and the a-plane sample at a higher 2.3-2.5 eV. As for the r-plane, it appears again to have the defect band centered lower in energy, around 2 eV.

Interestingly, in the NBE region (fig. 5.4), the free exciton (FX) at 3.377 eV can be observed for all samples, implying a good crystalline quality of the layers, as expected from MBE-grown material. Additionally, various donor-bound exciton lines can be observed, each sample having a different peak as the dominant level. An emission at 3.332 eV is observed on the lower side of the DX region only for the non-polar orientations. A peak at 3.31 eV is also observed in these samples, which has been sometimes attributed to stacking faults [77, 121]. However, there is no evidence of this defect being present in material such as the one here analyzed, being the origin of this line unclear. Indeed, this line, which has been labeled as α was observed in N-doped ZnO and is in reality a phonon replica of a line much higher in energy, due to Elastic Raman Scattering³. Therefore, lines β and γ are also identified as phonon replicas due to the same effect. Several broadening and shoulders appear in the spectra, possibly coming from phonon replicas of both the FX and the DX lower in energy spectra.

5.3 Intrinsic donors obtained by DLTS

As it was mentioned during the introduction of this chapter, the main objective is to analyze the presence of defects both close to the CB or the VB, and try to correlate them with their influence in the carrier concentration shown in fig. 5.2. In order to detect levels around the CB, DLTS was performed on the Schottky diodes processed on the three crystalline orientations. All the samples showed similar spectra, with the a- and m-plane orientations behaving, as in PL, in a similar way. A total of four defects at $E_C - 25 \text{ meV}$, $E_C - 100 \text{ meV}$, $E_C - 300 \text{ meV}$ and $E_C - 585 \text{ meV}$ were observed, with only the $E_C - 100 \text{ meV}$ and $E_C - 300 \text{ meV}$ being present clearly in all the samples. Indeed, they

³This issue is thoroughly analyzed in chapter 6.

Figure 5.5: DLTS spectra for the three samples for the $RW = 1000 \text{ s}^{-1}$ (left) and $RW = 20 \text{ s}^{-1}$ (center and right). Parameters: $t_{fill} : 50 \text{ ms}$, $V_{bias} : -1.5 \text{ V}$ and $V_{fill} : 0 \text{ V}$

correspond to the previously observed (chapter 1) E2 and E3 levels, respectively. Figure 5.5 shows the DLTS spectra for a rate window (RW) of 20 s^{-1} , with fig. 5.6 and table 5.1 summarizing the results.

Table 5.1: Deep levels obtained by DLTS close to the CB for the three samples, showing their concentrations (N_T) and capture cross sections (σ_n). The last row adds the total trap concentration close to the CB for each sample. Units: $N_T (\text{cm}^{-3})$, $\sigma_n (\text{cm}^2)$. *N.O. = Not Observed

Level (E_a) (meV)	m-plane		r-plane		a-plane	
	N_T	σ_n	N_T	σ_n	N_T	σ_n
$E_C - 25$	2×10^{15}	9×10^{-21}	N.O.*	N.O.*	3×10^{15}	9×10^{-21}
E2: $E_C - 100$	1×10^{15}	7×10^{-18}	$< 1 \times 10^{14}$	5×10^{-18}	5×10^{15}	8×10^{-18}
E3: $E_C - 300$	5×10^{14}	5×10^{-16}	5×10^{15}	6×10^{-16}	2×10^{15}	5×10^{-16}
$E_C - 585$	N.O.*	N.O.*	6×10^{13}	7×10^{-13}	N.O.*	N.O.*
$N_{total}^{CB} (\text{cm}^{-3})$	2×10^{15}		5×10^{15}		1×10^{16}	

The E2 and E3 intrinsic defects

The E2 level is dominant in the non-polar orientations, with concentrations of $1 \times 10^{15} \text{ cm}^{-3}$ for the m-plane and $5 \times 10^{15} \text{ cm}^{-3}$ in the case of the a-plane sample. It has a low cross section of $7 - 8 \times 10^{-18} \text{ cm}^2$, which makes it inefficient as a donor, despite its shallow energy. This level is also observed in the r-plane sample, but with a much lower concentration, below $1 \times 10^{14} \text{ cm}^{-3}$.

Indeed, for this sample, the dominant trap corresponds to the E3 level, also observed in the non-polar orientations. For the case of the r-plane, it has a concentration of $5 \times 10^{15} \text{ cm}^{-3}$, whereas the a- and m- planes have a concentration of $2 \times 10^{15} \text{ cm}^{-3}$ and $5 \times 10^{14} \text{ cm}^{-3}$, respectively. This defect, however, has a larger cross section, around

CHAPTER 5. DEEP LEVEL ANALYSIS OF HOMOEPITAXIAL ZNO IN NON-POLAR AND SEMIPOLAR ORIENTATIONS

$5 - 6 \times 10^{-16} \text{ cm}^2$, which makes it a more efficient defect. As it was reviewed in the section concerning the levels measured by DLTS in the literature (chapter 1), this E3 level has been observed consistently in ZnO, independently of the growth method. Many origins have been proposed, being H probably involved [48]. However, since all the samples were grown in the same environment (an MBE chamber without traceable H contamination), the only possible explanation is that H diffuses when the samples are exposed to the environment. A dual vacancy has also been proposed as a possible origin for this defect [21], which does not discard the involvement of H in its formation.

The deepest level at $E_C - 585 \text{ meV}$

Only in the semipolar sample a deeper level, with an activation energy of $E_C - 585 \text{ meV}$ is observed, albeit it having a low concentration ($\sim 6 \times 10^{13} \text{ cm}^{-3}$). This level also has a much larger cross section, around $7 \times 10^{-13} \text{ cm}^2$, so despite its deeper energy, could contribute to the CB population. As for its origin, although H has also been suggested to play a role, according solely to first-principles calculations [53], it could be an indication of the V_O defect, which has a low formation energy for n-type, Zn-rich material as is the one under consideration (chapter 1 and [53]).

The shallowest $E_C - 25 \text{ meV}$ donor

Yet, the most interesting result is the measurement of a very shallow level, at $E_C - 25 \text{ meV}$, only observed for the non-polar orientations. It could only be measured using large RWs, at energies which are clearly above freeze-out, but superimposed to the contribution from the E2 level. Therefore, only by aggregating measurements obtained from the FDLTS analysis, this emission could be uniquely distinguished.

Its concentration is large, similar to the E2 level, with the m-plane having $\sim 2 \times 10^{15} \text{ cm}^{-3}$ defects and the a-plane $\sim 3 \times 10^{15} \text{ cm}^{-3}$. It can easily be claimed that these concentrations are larger than those from the E2 level, and therefore this level should be blamed as the dominant defect. However, the cross section for this shallower defect is extremely low, about $9 \times 10^{-21} \text{ cm}^2$. This makes it less efficient as a donor, despite its shallower energy position.

Indeed, in both non-polar samples, a donor at an energy $\sim 25 \text{ meV}$ is observed by PL at room temperature, responsible for the dominant donor bound exciton peak. It is not difficult thus to state the correlation between the defect observed by electrical measurements and the DX luminescence from the optical spectra. Despite its low capture cross section (which by DLTS is the electrical value, not necessarily equal to the optical cross section), it has a high concentration and is very close to the band edge (less than one kT value), which can make it to be totally ionized at room temperature, and thus contribute powerfully to the photo-emission

The origin for this defect can be consistent with the level observed by Q-DLTS by Ton-That *et al* [137], which was related with the presence of H. Indeed, as it was indicated during chapter 1, shallow donors have been observed by different techniques, some of them related to H, which despite not being present during growth, can easily diffuse into the material later after exposure to the ambient.

Total trap concentration close to the CB

Adding up the total concentration of the defects close to the CB, a tentative *donor density* (N_{total}^{CB}) can be obtained, which is shown in the bottom line in table 5.1. Indeed,

Figure 5.6: Arrhenius plot for the DLTS and FDLTS measurements indicating all the observed levels.

it can be observed that the sample with the largest N_{total}^{CB} is the a-plane one, with nearly twice as many donor-like defects as the r-plane. The m-plane sample shows the lowest N_{total}^{CB} , suggesting that its reduced net carrier concentration obtained from CV measurements is not necessarily a result of compensation but a real reduction in the ionized donors.

5.4 Intrinsic acceptors obtained by DLOS

In order to analyze the presence of deep levels in the lower half of the bandgap, DLOS was performed in the three samples (fig. 5.7), obtaining several results which are summarized in table 5.2. It can easily be observed that the DLOS spectra is fairly similar between the three samples, with a larger trap concentration for the a- and r-plane samples. Again, this correlates with the findings of the CV measurements.

Three distinct levels are obtained close to the VB at $E_V + 0.25 \text{ eV}$, $E_V + 0.54/0.58 \text{ eV}$ and $E_V + 0.79 \text{ eV}$. As it can be observed in fig. 5.7, the $E_V + 0.25 \text{ eV}$ is dominant in all samples, with the capacitance rising until the excitonic or bandgap absorption dominates the conductance thus degrading the capacitance measurements. This level accounts for much of the total capacitance change.

Another defect at $E_V + 0.54 \text{ eV}$ is observed in the a- and r-plane samples, which is believed to have the same origin as the $E_V + 0.58 \text{ eV}$ defect obtained for the m-plane devices. The difference could come from the proximity of a filter change in that region of the spectra, which can induce errors in the onset identification. However, this level and the $E_V + 0.25 \text{ eV}$ one have been previously assigned to the V_{Zn} in measurements carried out in material grown by different methods [37, 45, 65, 66].

The deeper level at $E_V + 0.79 \text{ eV}$ is responsible for very little of the total capacitance change, although it could be clearly identified among all three samples. Its origin is unclear and no assignment has been made. Since during the whole DLOS measurement $\Delta C/C_0 \ll 1$, the obtained concentration values can be believed to be accurate, with the exception of the shallowest defect, for which the capacitance rise is truncated by the excitonic absorption.

Although no defects deeper in the bandgap could be clearly identified, the total capacitance change upon illumination with lower energies can be calculated, obtaining

CHAPTER 5. DEEP LEVEL ANALYSIS OF HOMOEPITAXIAL ZNO IN NON-POLAR AND SEMIPOLAR ORIENTATIONS

Figure 5.7: DLOS-SSPC spectra for the three ZnO orientations, with indication of the excitonic absorption, the bandgap and the relative positions of all the observed levels. Measurement parameters: T_{fill} : 30 s, $T_{transient}$: 300 s, V_{bias} : -0.5 V, V_{fill} : 0 V.

a value for the trap concentration further from the VB. These values can be observed in table 5.2.

Table 5.2: Summary of the labels obtained by DLOS for the three crystalline orientations. The total defect concentration close to the VB is also shown in the last row.

Level (eV)	m-plane N_T (cm^{-3})	r-plane N_T (cm^{-3})	a-plane N_T (cm^{-3})
$E_V + 0.25$	2×10^{16}	2×10^{17}	2×10^{17}
$E_V + 0.54/0.58$	5×10^{14}	5×10^{15}	3×10^{15}
$E_V + 0.79$	2×10^{14}	1×10^{15}	3×10^{15}
$> E_V + 0.79$	2×10^{15}	3×10^{16}	2×10^{16}
N_{total}^{VB} (cm^{-3})	3×10^{16}	2×10^{17}	2×10^{17}

Total trap concentration close to the VB

Similarly to what was done for the defects obtained by DLTS close to the CB, by adding up the concentration for the defects observed by DLOS, plus the total capacitance variation for energies below the first observable level, a value for N_{total}^{VB} (table 5.2) can be calculated for each of the samples. Both a- and r-plane samples show the same value of $\sim 2 \times 10^{17} cm^{-3}$, with the m-plane layers showing nearly an order of magnitude lower concentration.

5.5. THE INFLUENCE OF DEFECTS IN THE NET CARRIER CONCENTRATION

Table 5.3: Summary of the total concentration of traps close to the CB, VB, and the residual carrier concentration obtained from CV measurements (fig. 5.2).

	m-plane	r-plane	a-plane
$N_{total}^{CB} (cm^{-3})$	1×10^{15}	5×10^{15}	1×10^{16}
$N_{total}^{VB} (cm^{-3})$	3×10^{16}	2×10^{17}	2×10^{17}
$N_D^+ - N_A^- (cm^{-3})$	2×10^{16}	9×10^{16}	9×10^{16}
$N_{total}^{CB} - N_{total}^{VB} (cm^{-3})$	2×10^{16}	$\sim 2 \times 10^{17}$	$\sim 2 \times 10^{17}$

Figure 5.8: Summary of the total trap concentration at both sides of the bandgap, along with the residual carrier concentration.

5.5 The influence of defects in the net carrier concentration

In table 5.3 a summary of the previous findings is shown. It can be directly observed how the residual carrier concentration obtained from CV measurements directly correlates with the total trap density ($N_{total}^{CB} - N_{total}^{VB}$). It is important to remember, as was described in chapter 1, that the position of a defect close to a certain band does not directly target it as acting as a donor neither acceptor. However, in table 5.3, the total trap density has been calculated similarly to the net carrier concentration obtained from CV measurements, as the number of ionized donors (here, levels close to the CB) and ionized acceptors. Importantly, not every defect will be ionized at room temperature, since this process depends on both energy, cross section, and Fermi level position.

However, there is a clear indication that the reduction in net carrier concentration for the m-plane sample is due to a direct reduction in the trap density, and not a process of compensation by defects, as shown in table 5.3 and fig. 5.8. This indeed targets this orientation as the best candidate for device fabrication and the obtention of p-type material.

Figure 5.9: Bandstructure showing all the observed defects along with their assignment to defects and dopants in the material.

5.6 Conclusions

By combining CV, PL, DLOS and DLTS three different crystalline orientations in homoepitaxial ZnO have been characterized. In the PL spectra, at LT all orientations show a FX at 3.378 eV. In addition, the m- and a-plane show DX in the range of 3.375-3.357 eV with the dominant peak changing between samples. Resonant Raman scattering peaks, similar to that ones observed in N-doped material (chapter 6) are also observed, and responsible for the shoulders in the lower-energy PL spectra. At RT, the non-polar samples have the emission centered in a DX with a donor energy of 25 meV, consistent with the defect observed by DLTS at exactly that energy. This defect is not observed in the r-plane sample, and neither is it measured by DLTS, which can suggest a lowered concentration for this trap.

When analyzing the deep level spectra for these samples, close to the CB, in addition to the previously mentioned shallow defect at $E_C - 25 \text{ meV}$, two previously observed defects, the E2 and E3 levels, were measured. The shallow level was obtained only for the non-polar orientations, which had very similar trap distribution with the E2 level at $E_C - 100 \text{ meV}$ being dominant, and only having differences in the trap concentration. For the semipolar sample, the dominant level was the E3 at $E_C - 300 \text{ meV}$, without indication of the shallowest defects. Indeed, a deeper level was observed in this sample.

Close to the VB, all three samples were fairly similar, with the same three defects being present. Two of them could be related to the V_{Zn} and were previously observed in ZnO and related materials. Lastly, by analyzing the total trap concentrations both close to the VB and the CB, and correlating with the residual carrier concentrations measured by CV, it could be resolved that the reduction in net carrier density for the m-plane orientation is not the result of a compensation process, but a reduction in the total defect density. The trap concentration close to both bands is lower for the m-plane sample, and so is the net carrier concentration, indicating a higher crystalline quality of this orientation (5.8). Fig. 5.9 shows a bandstructure with all the observed energy levels, indicating their origin, as described during the chapter.

Chapter 6

Electrical mechanisms for carrier compensation in homoepitaxial nonpolar m-ZnO doped with nitrogen

This section is based on the published article "Electrical mechanisms for carrier compensation in homoepitaxial nonpolar m-ZnO doped with nitrogen" by A. Kurtz, A. Hierro, M. Lopez-Ponce, G. Tabares and J.M. Chauveau

Published in Semiconductor Science and Technology 31 (2016) 035010

Reference number: [65]

Presented at the Materials Research Society fall meeting 2014, celebrated in Boston, USA, November 30, 2014

6.1 Introduction

As it has been already explained in the introduction chapters of this thesis, there is clearly an unresolved issue regarding the presence of acceptor levels related with N, which compensate the material without reliably changing conduction from its intrinsic n-type to p-type. As it was reviewed, many reports of N-related acceptor levels observed by optical techniques can be found in the literature, but a direct electrical observation of the trap energy of the N-induced levels is required to uniquely identify the mechanisms leading to carrier compensation. Traditional Deep Level Transient Spectroscopy (DLTS) cannot be used to measure levels close to the VB in this type of material, requiring the use of optical excitation to generate minority carriers that become trapped at these shallow traps. Only one report from Muret *et al* [97] can be found for the case of N in ZnO, yielding activation energies (since the measurement is based on the thermal emission of carriers) and not direct trap energy levels. By using Deep Level Optical Spectroscopy (DLOS), these problems can be circumvented, since both direct trap energy and concentration values can be obtained for shallow traps close to the VB in n-type material.

Moreover, using high quality material with a low residual electron concentration is key to understanding the generation and role of acceptors, so that the net carrier concentration is low not because of auto-compensation by intrinsic defects, as previously

Figure 6.1: Schematic of the structure used for the devices in this study.

observed for MgZnO [45], but because of the presence of new acceptor levels introduced by the N dopant. Previous studies in MBE material report that non-polar orientations, especially m-plane homoepitaxially grown films, show the lowest residual carrier concentration with high crystalline quality and very low intrinsic defect and impurity concentrations [17, 18]. Thus, this chapter tries to shed light on the traps generated by N doping in homoepitaxial m-plane ZnO with low residual electron concentrations, grown under the best available conditions, in order to gain a complete picture of the electrical compensation mechanisms that result from N incorporation.

Sample description

Four samples were grown homoepitaxially by plasma-assisted Molecular Beam Epitaxy (MBE) on non-polar m-plane hydrothermal ZnO substrates from Tokyo Denpa. One sample was kept undoped (reference sample), whereas the three remaining samples were grown with increasing N concentrations (labeled during this study as low, mid and high N, respectively). From previous calibrations using SIMS under equal growth conditions and substrates [135], the N concentration in the films ranges from $\sim 10^{17} \text{ cm}^{-3}$ in the low N sample, to $\sim 10^{19} \text{ cm}^{-3}$ in the high N sample. The layer thickness was chosen to be large enough ($1.5 \mu\text{m}$) to attempt keeping the depletion region fully enclosed within the epilayer to try to avoid the electrical compensation of the films, as shown in fig. 6.1.

6.2 Impact of N in the optical signature

As a first step, the PL spectra was measured using continuous wave photoluminescence (PL) spectra were measured at low temperature (8K) using a 325 nm He-Cd excitation laser under a backscattering configuration and a 1 m monochromator. The low temperature (LT) spectra was analyzed (fig. 6.2), where two well distinct energy regions can be observed. The region at 3.36–3.37 eV shows sharp excitonic peaks in all films except for the highly doped one due to its lower crystalline quality. In this film, and as a result of its low PL intensity, a group of sharp peaks separated at a constant energy of 72 meV becomes evident. These peaks also affect the spectra of the mid N sample and appear at an integer number of the LO phonon energy (72 meV) below the laser pump energy (3.815 eV) as a result of resonant elastic Raman scattering. Indeed, the laser pump energy happens to be almost exactly $6 \times LO$ above the free exciton energy (3.377 eV). The dominant excitonic peaks that appear in the 3.36–3.37 eV region thus arise from

Figure 6.2: Photoluminescence spectra for the ZnO:N films at 8 K. In the mid and high N samples the peaks due to resonant elastic Raman scattering are indicated.

donor-bound excitons (DX) [90]. These excitonic emissions may arise both from the epilayer and from the ZnO substrate, especially in the undoped sample where the carrier diffusion length is expected to be much larger and the electron-hole pairs may reach the substrate and recombine there. In the N-doped samples, the fact that the DX emission decreases with increasing N concentration may be indicative that it does originate in the epilayer.

The major change in the PL spectra that results from N incorporation is the appearance of a prominent and broad donor-acceptor-pair (DAP) emission at 3.234 eV, with well defined LO phonon replicas (fig. 6.2) every 72 meV, in agreement with previous reports [70, 90, 135]. This DAP emission has a small blue shift as the N content is increased from the low to the mid N films and that is explained as a reduction in the donor-acceptor average separation [135]. In the high N sample the DAP is not clearly observed, but the broad weak PL signal is still centered at the DAP energy around 3.24 eV.

6.3 Electrical characterization

The Schottky diodes were processed using the techniques described in chapter 2. Basic electrical characterization consisted on the measurement of IV and CV profiles in the dark and at room temperature, in order to avoid persistent photo-induced effects. All the parameters were calculated using the custom software described in chapter 4, obtaining the Schottky barrier height (Φ_b), ideality factor (n) and series (R_s) and contact (R_c) resistances. CV profiles were measured both at 1 MHz using the Boonton 7200 capacitance meter, and at low frequency with the SR530 lock-in amplifier, obtaining the carrier concentration and conduction type. These parameters are summarized in table 6.1

Table 6.1 summarizes the results obtained from the IV profiles (fig. 6.3). The refer-

CHAPTER 6. ELECTRICAL MECHANISMS FOR CARRIER COMPENSATION IN M-ZNO:N

Table 6.1: Electrical characteristics from the Schottky diodes used for the capacitance measurements.

Sample	Ideality factor	Φ_b (eV)	R_s ($\Omega \cdot cm^2$)	R_c ($\Omega \cdot cm^2$)	$N_D^+ - N_A^-$ (cm^{-3})
Undoped	1.3	1.0	0.4	9.5×10^7	$\sim 1 \times 10^{16}$
Low N	1.2	1.2	6.1×10^1	4.2×10^9	$\sim 2 \times 10^{15}$ (10 kHz)
Mid N	2.4	1.1	1.6×10^2	2.3×10^9	depleted
High N	2.8	1.1	1.1×10^3	4.1×10^9	—

Figure 6.3: Current-voltage (IV) characteristics of the diodes measured under dark conditions.

ence sample showed a Schottky barrier height around 1 eV, rising slightly to 1.1–1.2 eV for the N-doped samples. The ideality factor increased from 1.2–1.3 to 2.8 with N concentration, implying a reduced quality of the Schottky diode. The series resistance (R_s) is limited, among other things, by the resistivity of the material, and rises linearly with the N incorporation (table 6.1), which indicates an increased electrical compensation. The undoped (reference) sample has an $R_s = 0.4 \Omega \cdot cm^2$, whereas with a low N incorporation, it rises to $61 \Omega \cdot cm^2$. The mid N sample shows a further increase in resistance up to $1.6 \times 10^2 \Omega \cdot cm^2$, reaching a maximum value for the high N of $1.1 \times 10^3 \Omega \cdot cm^2$. The contact resistance (R_c) rises from $\sim 10^8 \Omega \cdot cm^2$ in the undoped sample to a stable value between $2\text{--}4 \times 10^9 \Omega \cdot cm^2$, indicating a reduced effect of N in the ohmic contact quality.

The CV profiles both at 1 MHz and 10 kHz for all films are shown in fig. 6.4-a, in addition to the resulting carrier concentration vs depth profiles (fig. 6.4-b). These profiles show that the undoped sample has a net carrier concentration around $\sim 1 \times 10^{16} cm^{-3}$ and a depletion region that lays completely inside the grown layer. The low N sample shows a similar residual carrier concentration to the reference sample at 1 MHz, although it decreases to $\sim 2 \times 10^{15} cm^{-3}$ when reducing the probing frequency to 10 kHz. This effect suggests a low efficiency of the compensating acceptors, as will

Figure 6.4: Capacitance-voltage profiles (a) and carrier concentration profiles (b) measured in the dark for the undoped, low N and mid N samples. Measurements were carried out both at 1 MHz –solid symbols in (a)– and 10 kHz –open symbols in (a)–. The inset in (a) shows the CV profile under 3.2 eV illumination for the mid N sample, and the resulting carrier concentration is shown in (b).

be explained in a later section of this paper.

The mid N sample could not be effectively measured in the dark, due to the high compensation that totally depletes the grown layer at 10 kHz, as can be observed in fig. 6.4-b. However, under illumination above the mid-gap (concurrent with the start of the DLOS spectra), the depletion width shrinks sufficiently and the CV can be effectively measured, giving an electron concentration of $\sim 1 \times 10^{16}\text{ cm}^{-3}$. This value will be used on the trap concentration calculations for this sample, since it is more accurate than the one measured in the dark, because the capacitance values used in equation 2.49 are obtained with DLOS, i.e., under illumination. Indeed, and in order to clarify the region being probed by DLOS, a CV spectra under 3.2 eV illumination is shown in fig. 6.4-a, where it can be observed that the depletion layer is confined entirely in the epilayer, yielding a value of $1.3\text{ }\mu\text{m}$. Moreover, by calculating the Debye screening length (around 25 nm, eq 2.27), the obtained value can be considered an accurate estimation of the real depletion depth [58]. It also has to be stated that despite the illumination and low frequency measurements, this sample did not show the MIS-like shape in its CV curves, indicating a very thin layer, and making the measurements reliable considering the model from chapter 3 [67].

The high N sample was so heavily compensated, as indicated by the large series resistance (table 6.1), that its capacitance remained unchanged under any bias or illumination conditions. Thus, this sample was fully depleted and could not be analyzed by DLOS.

6.4 Deep level optical spectroscopy measurements

DLOS spectra were obtained using the equipment described in chapter 4, controlled with a fast optical shutter. All measurements were carried out at 1 MHz, since the quality factor under illumination was good enough ($Q > 1$), and by using a high probing frequency the signal to noise ratio (SNR) is increased. However, the noise level was still

Figure 6.5: DLOS spectra for the undoped (a), low N (b) and mid N (c) samples at 1 MHz and room temperature. The figure right of (c) shows the normalized photocapacitance spectra from the mid N film measured with and without an electrical fill pulse.

large and no photocapacitance transients could be recorded, thus limiting the study to the steady state photocapacitance (SSPC). The diodes were illuminated at each energy for 300 s under reverse bias conditions ($V_{bias} = -0.5$ V), and then the steady state value of the photocapacitance (C_{ss}^{photo}) was recorded during illumination. A 30 s-long filling pulse in the dark at 0 V was used between consecutive energy steps. All the measurements were carried out at room temperature.

Figure 6.5 shows the SSPC spectra for the three samples that were electrically measurable (undoped, low N and mid N). It can be observed how both the undoped and low N samples show a significant decrease of photocapacitance above the exciton energy (~ 3.31 eV). Indeed, a large increase in photogenerated carriers raises the conductivity of the diode, thus degrading the quality factor for the capacitance measurement, affecting the measured capacitance value ($Q < 1$). Nevertheless, and regardless of the presence or absence of N, all three samples show a level at $E_V + 0.25$ eV, which for the reference and low N samples is the only trap that can be uniquely resolved.

In the case of the undoped sample, several levels show up deeper in the bandgap (fig. 6.5-a). However, they cannot be resolved due to the high sensitivity to illumination of the recorded SSPC spectra, which mixes the signatures from the levels with the lamp intensity variations arising from the Xe discharge lines. These levels account for nearly half of the total capacitance change of the sample, i.e., for the total trap concentrations. Using the carrier concentrations from the CV analysis, and by applying equation 2.51, a lower bound trap concentration for the $E_V + 0.25$ eV level of $\sim 1.4 \times 10^{16} \text{ cm}^{-3}$ is obtained, being the rise in photocapacitance affected by the degradation in the quality factor because of the excitonic absorption.

As for the low N sample, the aforementioned levels deep in the bandgap can hardly

be observed, suggesting a reduction in their concentration with N incorporation. In this sample, only the level at $E_V + 0.25 \text{ eV}$ is clearly observed (fig. 6.5-b), as in the reference sample. Similarly, a degradation in the quality factor for the capacitance measurement appears above the excitonic absorption energy. Therefore, the concentration for the trap is only a lower bound, giving a very similar value of $\sim 1.2 \times 10^{16} \text{ cm}^{-3}$.

In the mid N sample, the $E_V + 0.25 \text{ eV}$ level is still observed but its trap concentration cannot be easily calculated due to the close proximity of a new level (fig. 6.5-c), which masks the associated rise. Considering the small increase this level generates in the spectra, an approximate defect concentration of $\sim 4 \times 10^{14} \text{ cm}^{-3}$ is obtained. However, it is important to note that because of the high electrical compensation already mentioned for the sample, the depletion region remains unchanged until a trap with a concentration high enough is photoexcited, causing an increase in the carrier concentration and a reduction of the depletion region width. Under these conditions the diode capacitance starts to be measurable, as it can be clearly observed in fig. 6.5-c, in which $\Delta C/C_0$ has risen already to a value of 0.02 at the start of the first distinguishable level ($E_V + 0.48 \text{ eV}$). This is a direct indication that the steady state value of the photocapacitance (C_{ss}^{photo}) has changed respect to the dark value (C_0), which indicates that the depletion region width is being modulated, and thus the epilayer is no longer frozen out as it was under dark conditions. Therefore, the notion that more levels are present deeper in the bandgap cannot be discarded. This may be the reason why the energy level associated with the N_O substitutional, which should be present at $\sim E_V + 1.2 \text{ eV}$ [86, 89, 135, 136], is not observed. It is also important to note that in DLOS all traps found within the depletion region and below the Fermi level contribute to the photocapacitance, independent to their distance from the depletion region edge. In our samples, the Fermi level is above the midgap, and the Schottky built-in voltage ($\sim 1 \text{ V}$) plus the applied bias (0.5 V) is lower than half the bandgap. Thus, the contribution of the photoexcited traps (all found close to the valence band) to the photocapacitance is present from the depletion edge up to the surface, being the space charge region located entirely in the epilayer.

The most interesting result related to the N incorporation is the presence of three new traps that show up in the spectra under illumination energies of $E_{photon} = 2.89 \text{ eV}$ ($E_V + 0.48 \text{ eV}$), 3.20 eV ($E_V + 0.17 \text{ eV}$) and 3.25 eV ($E_V + 0.12 \text{ eV}$). The level at $E_V + 0.48 \text{ eV}$ is clearly not present in the reference sample without N. By using equation 2.51, its concentration can be calculated to be $\sim 1 \times 10^{14} \text{ cm}^{-3}$, which is very small compared to the incorporated N concentration, albeit related to it. However, this concentration must be taken as a lower bound, since, as we mentioned earlier, the sample is depleted in the dark and for lower illumination energies, and the total change in capacitance can be easily underestimated. As will be explained in the discussion, this level has already been observed using DLOS in N-doped MOCVD-grown MgZnO, as shown in [66] (chapter 7).

The next N-induced trap appears in the SSPC spectra as a decrease in capacitance change at $E_{photon} = 3.20 \text{ eV}$ (fig. 6.5-c), only when a voltage fill pulse of 0 V is applied as detailed in the experimental section. When the DLOS spectrum is recorded without a voltage fill pulse, i.e. under a constant -0.5 V reverse bias, this negative step disappears (fig. 6.5-c, inset). Thus, we conclude that the voltage fill pulse is responsible for the negative step. This can be understood as a result of the competition between the majority (electron) carrier photoemission to the CB and minority (hole) carrier thermal emission to the VB [19]. Indeed, its shallow position with respect to

CHAPTER 6. ELECTRICAL MECHANISMS FOR CARRIER COMPENSATION IN M-ZNO:N

the VB ($E_V + 0.17\text{ eV}$) is consistent with thermal hole emission to this band at RT. Since the sample is fully depleted in the dark, a significant amount of holes may exist to compensate the material, which can be trapped during the electrical fill pulse. Thus, we can conclude that this negative onset can be related to a hole trap found at $E_V + 0.17\text{ eV}$.

The shallowest trap, linked to the last onset observed in the SSPC spectrum, is located at $E_V + 0.12\text{ eV}$ and accounts for most of the capacitance change shown by this sample. Using equation 2.51, a trap concentration of $\sim 1.2 \times 10^{15}\text{ cm}^{-3}$ is obtained, which is still over three orders of magnitude lower than the N concentration in the sample. Since this trap is also the shallowest among all the traps with respect to the VB, it is key to understanding the effect that the growth under N has on these homoepitaxial films.

6.5 N-related and intrinsic acceptors

From the combination of PL, CV and DLOS it can be observed that N plays an important role in the deep level distribution, reducing the intrinsic carrier concentration, but without achieving p-type conductivity. Next, we review all of the electrically observed traps, their relation to the PL bands, and their potential physical origin, according to the levels previously found in the literature that were summarized in chapter 1.

6.5.1 The intrinsic $E_V + 0.25\text{ eV}$ trap

In all samples, including the N-free reference sample, a trap at $E_V + 0.25\text{ eV}$ is observed, indicating that it is not related to N, which suggests an intrinsic defect that is responsible for the whole capacitance change close to the VB. As has already been described, for the undoped and low N samples, determining the concentration for this trap is largely affected by the excitonic absorption that degrades the capacitance measurement by increasing the conductivity. Nevertheless, a lower bound trap concentration of $\sim 1.4 \times 10^{16}\text{ cm}^{-3}$ is obtained. This trap matches the hole trap reported by Muret *et al* [97] at $E_V + 0.28\text{ eV}$ (labeled HT4 in his paper) in N-doped ZnO samples, using optical minority carrier transient spectroscopy (O-MCTS). In their work they suggest that this hole trap is not related to N, since its Arrhenius plot matches well with that from a similar level observed in undoped samples by other groups. Their measured defect concentration, $\sim 2 \times 10^{16}\text{ cm}^{-3}$, agrees quite well with our measured trap concentration ($\sim 1.4 \times 10^{16}\text{ cm}^{-3}$), clearly showing that this level is the dominant intrinsic trap close to the VB in m-ZnO. The difference in energy between HT4 ($E_V + 0.28\text{ eV}$) and our result ($E_V + 0.25\text{ eV}$) could arise from the experimental error bar as well as the fact that DLOS yields the actual trap energy in the bandgap, whereas O-MCTS yields the activation energy that assumes, among other things, that the trap capture cross section is temperature independent [12].

Zinc vacancies have been proposed as an intrinsic defect creating a level with a very similar energy. Janotti *et al* [53] calculated this level to have a transition energy ranging 0.08–0.45 eV from the VB, depending on the calculation method. More recently, Bang *et al* [11] calculated this transition to be $E_V + 0.17\text{ eV}$. In their review, the intrinsic V_{Zn} defect is more likely to be found in O-rich samples, with a much shallower energy (closer to VB [53, 56, 62]) and lower formation energy. However, since these energies come from different calculation methods and conditions, their value must be taken with caution. Moreover, Hierro *et al* [45] also reported a level at $E_V + 0.28\text{ eV}$ in undoped MgZnO grown by MOCVD in sapphire substrates that is responsible for the compensation measured in the samples, showing a large defect concentration. Gür *et al* [37] also found a level at $E_V + 0.3\text{ eV}$ in both ZnO and MgZnO films grown by

MBE on sapphire. This level was, as in our case, the dominant onset in the DLOS spectra, driving the majority of the capacitance change, further confirming the common intrinsic origin for the trap. In addition, the results from chapter 5 show that this level is present in undoped homoepitaxial ZnO grown in a- and r- planes, which combined with the former reports, indicates that a level at $E_V + 0.25\text{ eV}$ is indeed an intrinsic level independent of the growth method and substrate orientation.

6.5.2 The N-induced $E_V + 0.48\text{ eV}$ trap

This trap starts to be observable in the mid N sample suggesting a relationship with N incorporation. Moreover, its concentration is quite low, $\sim 1 \times 10^{14}\text{ cm}^{-3}$, indicative of a reduced impact in the electrical compensation shown by this sample. Several levels have been previously reported by Muret *et al* [97] by O-MCTS with similar trap energies. Their HT5 level yields an equal energy of $E_V + 0.48\text{ eV}$, although with a much higher concentration value. However, and because of the error bar, our level could also correspond to their HT6 or HT7 traps, with energies of $E_V + 0.466\text{ eV}$ and $E_V + 0.503\text{ eV}$, respectively. Also, a previous report from our group [66] shows a similar trap at $E_V + 0.47\text{ eV}$ in MOCVD-grown $\text{Zn}_{0.9}\text{Mg}_{0.10} : \text{N}$ films measured by DLOS, whose concentration increases with increasing N incorporation during growth.

6.5.3 The N-induced $E_V + 0.17\text{ eV}$ trap

The level at $E_V + 0.17\text{ eV}$ is only observable as a reduction in the overall capacitance in the DLOS spectra. As already explained in the previous sections, the thermal emission of trapped holes to VB dominates over the trapped electron photoemission to the CB, producing a decrease of the total measured capacitance. Unfortunately, this competition of emission mechanisms does not allow the quantification of its trap concentration [12, 16], but it does imply that the defect behaves as a minority carrier trap, in this case, a hole trap.

The energy measured by DLOS is consistent with the acceptor involved in the N-related DAP emission we observe in the LT-PL (fig. 6.2) spectra, for which there is a consensus that it is found at 165 meV above the valence band [70, 129, 135, 151, 154]. In addition, Muret *et al* [97] reported a level at $E_V + 0.19 \pm 0.04\text{ eV}$, labeled HT2, with a large capture cross section, related to N incorporation. Thus, this trap at $E_V + 0.17\text{ eV}$ can be linked to the N-induced DAP. We should note that this level can only be observed by DLOS in the mid N sample, although it is also likely to be present in the low N sample. However, because of the large rise in capacitance from the dominant intrinsic $E_V + 0.25\text{ eV}$ level, it may not be possible to detect the trap, even though the DAP emission to which it contributes is clearly present in the LTPL spectra (fig. 6.2). In previous work from our group [66], a level at $E_V + 0.16\text{ eV}$ was reported in MgZnO films, with a defect concentration increasing with N incorporation during growth, and related to the electrical compensation observed in the samples.

There is an open question about what is the physical origin for the acceptor that appears with the introduction of N. In the literature, many possible N configurations in ZnO have been described, although great discrepancy can be found in the calculated energy position of the acceptors they generate, which depend on the calculation method. In the review by Bang *et al* [11], a revision of the most plausible levels related to N incorporation is presented, which provides a new canvas for the analysis of the acceptor-like levels found in N-doped ZnO samples. The simple substitutional N_O level has a

CHAPTER 6. ELECTRICAL MECHANISMS FOR CARRIER COMPENSATION IN M-ZNO:N

large activation energy, it is present deep in the bandgap [86, 136] and is also unlikely to appear in such O-rich samples as the ones presented in this paper, since formation energy increases with O-richness. Thus, it can be discarded.

In a previous section, the V_{Zn} -related level defect is proposed to be present in the N-doped samples and although it is the only level not related with the presence of N during growth it is needed for the formation of many of the other levels proposed as acceptors. Indeed, the $N_O - V_{Zn}$ complex defect proposed by Liu *et al* [78] with an energy level of 160 meV above the VB, may be related to the $E_V + 0.17\text{ eV}$ trap. For this complex defect a thermal activation is needed, which in our case could be provided by remaining at the growth temperature [135] during the growth time needed to reach 1.5 μm -thick layers (more than 5 h). However, Bang *et al* [11] suggested that the $N_O - V_{Zn}$ complex has a paramagnetic nature that, when taken into account in the calculation, yields a much deeper trap energy in the bandgap ($E_V + 0.87\text{ eV}$).

Three defects involving a molecular form of N have also been proposed in the literature. The simplest one, $(N_2)_{Zn}$, with an activation energy of $E_V + 0.22\text{ eV}$ is also the one with the largest formation energy [11]. It is thus unlikely to be the defect responsible for any of the N-related levels found in the present study. Another one, involving oxygen, $(N_O)_{Zn}$, shows a much lower formation energy with a similar activation energy ($E_V + 0.23\text{ eV}$). Lastly, the level with the lowest formation energy, $(NH_4)_{Zn}$, has an energy of $E_V + 0.18\text{ eV}$, but needs the presence of large quantities of H, which is not the case for the samples presented in this paper, grown by MBE using N_2 as the dopant source.

6.5.4 The N-induced $E_V + 0.12$ trap

The new level at $E_V + 0.12\text{ eV}$ is not directly observed in the PL spectra, albeit being dominant in the phot capacitance measurement for the mid N sample. However, to understanding its origin one has to account for the spatial effects that arise from the fact that this sample is depleted in the dark, and only under illumination can the depletion region be slightly modulated with the AC probe signal. Thus, the region being measured during DLOS is close to the substrate/epilayer interface, and the DLOS spectra can be influenced by the presence of structural defects originating at this interface. In order to fully distinguish the type of defect involved, minority carrier DLTS using a variable fill pulse may be needed, as reported by Hierro *et al* [43], where different kinetics for point defects, extended defects, and point defects decorating the extended defects can aid in this identification. Also, depth sensitive measurements could help clarify the structural origin of this defect. Unfortunately, both types of measurements cannot be performed in a film so strongly depleted like ours.

Accounting exclusively for its energy position in the bandgap, the $E_V + 0.12\text{ eV}$ trap may be related to stacking faults. Indeed, Lautenschlaeger *et al* [71] showed that a PL band at 3.31 eV appeared when N is introduced in ZnO, and in parallel to the formation of the DAP. Their emission is likely to be the same as that shown by Schirra *et al* [121] to arise from a band-to-acceptor recombination (e, A). The acceptor level involved in this emission was proposed to be generated by stacking faults and placed at $E_V + 0.13\text{ eV}$, very close to the level observed in our films. Lin *et al* [77] clearly demonstrated that in m-plane ZnO films stacking faults are responsible for the presence of a CL band at 3.32 eV. However, we do not observe this stacking fault-related emission in our films, and thus, it is unlikely that they are related. Even though the $E_V + 0.12\text{ eV}$ trap concentration is quite low, $\sim 1.2 \times 10^{15}\text{ cm}^{-3}$, this trap shows a sharp optical onset

Figure 6.6: Bandstructure summarizing the observed defects for the undoped and low N samples (left) and mid N one (right), indicating the origin. N-related defects are highlighted in red.

dominating the DLOS spectra, and it is clear that unveiling its physical origin will likely open the path to understanding how N is incorporated in the crystal.

6.6 Conclusions

From the combination of PL, CV and DLOS we have shown that the incorporation of N produces a strong electrical compensation, decreasing the measured electron carrier concentration from $\sim 1 \times 10^{16} \text{ cm}^{-3}$ down to $\sim 2 \times 10^{15} \text{ cm}^{-3}$. Under very high N incorporation ($\sim 10^{19} \text{ cm}^{-3}$) the $1.5 \mu\text{m}$ -thick films are actually fully electrically depleted and cannot be analyzed. As summarized by fig. 6.6, this decrease in the electron carrier concentration with N incorporation happens in parallel to the formation of three new traps at $E_V + 0.48 \text{ eV}$, $E_V + 0.17 \text{ eV}$ and $E_V + 0.12 \text{ eV}$, in addition to the $E_V + 0.25 \text{ eV}$ intrinsic level that is also found without N and that is likely to be related to V_{Zn} . This intrinsic level also dominates the DLOS spectrum under low N concentration, where a DAP band is clearly observed in the LT-PL that is also prominent in the mid N film. However, in the mid N film the new set of three shallow traps with respect to the VB can clearly be resolved by DLOS and their energy position in the bandgap perfectly placed. The $E_V + 0.45 \text{ eV}$ trap correlates well with a similar trap observed in MOCVD-grown MgZnO [66] (chapter 7). The $E_V + 0.12 \text{ eV}$ trap is the shallowest and its presence can be clearly distinguished from that of the $E_V + 0.17 \text{ eV}$ in the DLOS spectra, and indeed both traps can be linked to different sources. First, the $E_V + 0.12 \text{ eV}$ trap does not correlate with any PL bands, but shows the highest defect concentration of all traps ($\sim 1.2 \times 10^{15} \text{ cm}^{-3}$). Its significance in the DLOS spectra and its shallow position in the bandgap suggest that this level is crucial to understanding the micro-structural changes induced by N incorporation. In contrast, the $E_V + 0.17 \text{ eV}$ trap behaves as a minority carrier trap producing a capacitance signature consistent with hole emission to the valence band, and may originate at $N_O - V_{Zn}$ complexes [78]. It is also almost certainly the acceptor level involved in the N-induced DAP emission observed in the LT-PL, widely accepted to be at $E_V + 0.165 \text{ eV}$ [70,77,129,135,151,154], and this correlates well with an electrically observed trap in N-doped MgZnO at a similar energy [66].

Chapter 7

Acceptor levels in MgZnO:N

This section is based on the published article "Acceptor levels in MgZnO:N probed by deep level optical spectroscopy" by A. Kurtz, A. Hierro, E. Muñoz, S. K. Mohanta, A. Nakamura, and J. Temmyo

Published in Applied Physics Letters 104, 081105 (2014)

Reference number: [66]

Presented at the 16th International Conference on II/VI Compounds and Related Materials, celebrated in Nagahama, Japan, on September 9, 2013

7.1 Introduction

As it was presented in chapter 1, understanding the mechanisms for p-type doping in ZnO still remains as one of the key factors that block the full development of ZnO optoelectronics [9]. Even though p-type doping seems limited by the problem of the doping asymmetry [156], there have been substantial advances identifying potential paths for efficient hole generation. Among the many proposals, for the case of N doping, complex defects, such as the $V_{Zn} - N_O$ proposed by Liu et al. [78], might act as an efficient acceptor in ZnO. This acceptor may have an activation energy of 160 meV, which could lead to reliable p-type conductivity. Indeed, Muret et al. [97] identified two acceptor-like deep levels in molecular beam epitaxy (MBE) grown ZnO:N at $E_V + 0.485\text{ eV}$ and $E_V + 0.19\text{ eV}$, which may be related to the N_O and the $V_{Zn} - N_O$ complex, respectively. The low activation energy of the shallowest acceptor-like level indicates that it can be fully ionized at room temperature, and thus may efficiently inject holes into the valence band (VB).

Recalling chapter 1, it can be remembered that for the case of metal organic chemical vapor deposition (MOCVD) grown ZnO:N, Reynolds et al. [119] also recently observed the presence of an acceptor level with an activation energy of 150 meV, and have proposed that a $V_{Zn} - N_O - H$ complex is responsible for its generation. Alternatively to ZnO, many groups have used MgZnO for the p-side of their p-n junctions, [40,149] among other reasons because MgZnO presents lower residual electron carrier concentrations than ZnO [37,45,75]. Indeed, with Mg compositions around 10% it may be easier to obtain p-type conductivity using N as an acceptor [93,94]. Thus, the aim of this chapter is to analyze the impact of N in the formation of deep levels close to the valence band of $Zn_{0.9}Mg_{0.1}O$, by means of DLOS and LCV, as explained in chapter 2.

Figure 7.1: Schematic for the device structure used during this study.

 Figure 7.2: IV curves for the Au-Zn_{0.9}Mg_{0.1}O:N diodes. The inset shows the normalized PL spectra of the three films.

7.2 Compensation by N incorporation

Three Zn_{1-x}Mg_xO samples were grown on c-plane orientation (a-plane sapphire [11-20]) by remote plasma enhanced MOCVD at 400° C in the presence of a N₂ flow of 5 sccm and under O-rich conditions with thicknesses in the range of 1.3 – 0.6 μm , enough to ensure that the depletion region lays entirely inside the epilayer (fig. 7.1). [93, 94] In order to ensure that the exposure to N was the only parameter being changed among the samples, they were all grown during the same run. The sample position in the reactor was used to control the amount of N concentration: the high N sample was placed closer to the N source, mid N further from it, and low N the furthest of the three. Mg is introduced in order to reduce the carrier compensation by reducing the efficiency of the intrinsic donors by making them deeper [138]. The nominal Mg composition was chosen to be 10%, since we have previously shown that this value is a good compromise between strong carrier compensation and material quality. [45, 93] In order to confirm that the different sample position did not affect the incorporation of Mg, photoluminescence (PL) spectroscopy

7.3. DEEP LEVEL OPTICAL SPECTROSCOPY SIGNATURES OF N DOPING

Figure 7.3: SSPC spectra for the three $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}:\text{N}$ films.

measurements were carried out, showing that all samples had a similar band gap of ~ 3.42 eV [93] (inset of Fig. 7.2). Previous results in similar layer show good crystalline quality measured by structural techniques [99]. Schottky diodes were processed on the samples by means of the procedure described in chapter 2. As it will be shown in a following section, this treatment may generate a thin insulator layer between the metal and the semiconductor [94,100], that can affect the capacitance measurements. Indeed, the creation of this layer is widely enhanced by the high surface roughness of the samples, creating MIS structures (fig. 7.1). These diodes showed reasonable rectification (Fig. 7.2) and a leakage current low enough to allow for the capacitance measurements to be performed.

7.3 Deep level optical spectroscopy signatures of N doping

It has been already explained how one of the major difficulties when detecting acceptor-like levels close to the VB in n-type material arises from the fact that minority carriers are needed, and thus, techniques like DLTS are more limited. To circumvent this problem, DLOS [16] has been used, allowing the observation of N-related deep levels close to the VB. The lock-in amplifier plus a wave function generator were used to measure the diode capacitance and conductance, as described in chapter 4. The sample was kept at a constant $V_{\text{bias}} = -0.5$ V with a 50 mV_{pp} AC signal, after waiting more than 100 hours in the dark in order to avoid persistent photocapacitance effects. All the measurements were carried out at room temperature.

The choice of a low probing frequency during the photocapacitance measurement is very important in this type of material, since deep levels may have a slow response. However, a high frequency is also desired in order to increase the signal to noise ratio. In our case, the large series resistance observed in the three samples (Fig. 7.2) leads to a large time constant which limited the maximum measurement frequency to values below 100 kHz. In addition, a low parallel resistance was observed at low frequencies (< 1 kHz) leading to an increased diode conductivity limiting the viability of a capacitance measurement. Because of these limitations, all the capacitance measurements

Figure 7.4: Left: Onsets in the SSPC spectra for the three films that determine the observed trap energy. Right: LCV profiles for the samples at different representative photon-energies.

were carried out at 10 kHz, achieving acceptable quality factors(Q). The DLOS spectra were obtained under steady-state conditions (steady state photocapacitance - SSPC) by recording the photocapacitance values 300 seconds after illumination. A 30 s-long fill pulse in the dark was used with the bias kept constant. The SSPC spectra for the three samples can be observed in Fig. 7.3.

Interesting to note is that the total capacitance change due to the deep levels, $\Delta C/C_0$, correlates among the three samples with the N concentration (Fig. 7.3), suggesting that deep levels with increasing concentrations have been generated as a result of the larger N incorporation. As it will be explained below, the behavior of the measured CV curves during illumination can be well explained with the model of a metal-insulator-semiconductor (MIS) diode on n-type material with accumulated holes at the insulator/MgZnO interface. This implies that the onsets observed in the SSPC spectra correspond to deep levels initially filled with electrons that are photoexcited to the conduction band (CB) during illumination. Thus, the large changes in $\Delta C/C_0$ observed in Fig. 7.3 are due to energy levels close to the VB that when emptied yield a positive charge increase in the depletion region.

As shown in Fig. 7.4-left, three main energy onsets have been observed in the

7.4. TRAP CONCENTRATIONS BY LIGHTED CV PROFILING: THE MIS EFFECT

SSPC spectra of the samples which correspond to trap energies of $E^{T1}=E_V + 0.16\text{ eV}$, $E^{T2}=E_V + 0.35\text{ eV}$ and $E^{T3}=E_V + 0.47\text{ eV}$ eV. As shown in Table 7.1, the $\Delta C/C_0$ steps generated by the T2 and T1 levels, closest to the VB, are much larger than that of T3, and therefore more likely to be responsible for carrier compensation and possibly hole generation. While T2 is clearly measured among all samples, T1 cannot be observed in the high N sample, perhaps because it is masked by the high capacitance rise due to T2 (Fig. 7.4-left). Overall, the $\Delta C/C_0$ steps scale with the N concentration in all samples. However, the trap concentration (N_T) cannot be directly quantified from the $\Delta C/C_0$ steps because $\Delta C/C_0 \geq 1$ for most traps, which implies that upon photoexcitation of the traps there is a large change in the depletion space charge.

7.4 Trap concentrations by lighted CV profiling: the MIS effect

This effect was described in chapter 2, and can be circumvented by using lighted capacitance voltage (LCV) [3], in order to quantify N_T based on the fact that under below-bandgap illumination the net carrier concentration in the diode is changed due to the de-trapping of all trapped carriers from the deep levels being photoexcited. Thus, standard CV profiles were measured for all samples under photon energies chosen from the SSPC spectra to be slightly below and over the activation energies for each observed trap. [3, 45]

The resulting LCVs (Fig. 7.4-right) present shapes that do not correspond to the model of a Schottky diode, especially under large photon energies, and thus the net carrier concentration cannot be directly derived from them. In fact, the capacitance increase with reverse bias when the diodes are illuminated could mistakenly suggest that the material is p-type. However, a detailed analysis of the curves indicates that a metal-insulator-semiconductor (MIS) contact can be responsible for the observed shapes of the CVs. [37] This is consistent with the fact that the H_2O_2 treatment may generate a thin ZnO_2 film prior to the Schottky metal deposition. [61, 100]

In chapter 1, it was explained that in an MIS diode, the total measured capacitance is a series combination of the insulator (C_{ins}) and the depletion (C_{dep}) layer contributions (fig. 1.16). Within this model, the shape of the measured LCV profiles corresponds to a MIS diode on n-type material measured at low frequencies. [132] Thus, an accumulation of holes (inversion charge) appears at the insulator/MgZnO interface as a result of the band bending. The decrease of the lighted capacitance curves for larger reverse biases could be the result of a degraded Q-factor of the capacitance measurement, which may result from enhanced tunnel current through the insulator.

During the DLOS measurements, while illuminating with energies below bandgap, no minority carriers are generated, and the inversion charge remains unchanged since the bias is kept constant. Therefore, the deep levels found in the bulk of the material within the depletion region are photoexcited causing an onset in the SSPC spectra (Fig. 7.4-left). Only when the photon energy is larger than the bandgap, there is a large generation of minority carriers (holes in this case), and the inversion charge increases as a result of hole trapping at the insulator/MgZnO interface. This effect is evident in the mid N and low N samples. In both cases, when the diodes are illuminated above bandgap the total measured capacitance increases quite notably (Fig. 7.4-left). This is contrary to what happens in a regular Schottky diode, where the maximum change in capacitance in a SSPC spectrum always happens just resonant with the bandgap, [44]

since the photogenerated minority carriers are lost to the metal and do not generate a capacitance change during above bandgap illumination. In the case of the high N sample, the change in depletion capacitance is so large as a result of large trap concentrations that this effect is not observed.

According to theory of a MIS diode (chapter 1), the bulk net carrier concentration ($n = N_D^+ - N_A^-$) can be obtained from the minimum in the CV curve (C_{min} , eq. 3.2), where the inversion layer is not formed, and by taking into account the effect of the insulator as a capacitor in series with the depletion region:

$$C_{min} = \frac{C_{ins} \cdot C_{dep}^{max}}{C_{ins} + C_{dep}^{max}}$$

where:

$$C_{dep}^{max} \simeq \epsilon_s \left(q^2 \frac{(N_D^+ - N_A^-)}{4\epsilon_s kT \ln \left(\frac{(N_D^+ - N_A^-)}{n_i} \right)} \right)^{1/2} \quad (7.1)$$

The insulator capacitance (C_{ins}) is unknown in our case and can only be assumed to be equal or greater than the highest observed capacitance for any diode from this study under a large reverse bias ($C_{ins}=461$ pF), since the H_2O_2 treatment was the same for all samples and diodes. In Ref. 16 a similar surface treatment was shown to generate a 20 nm-thick ZnO_2 layer on ZnO samples. Using the dielectric constant of ZnO, the insulator capacitance would be 800 pF, which is of the order of magnitude of the values observed by LCV. Using this model (Eq. 7.4), the carrier concentrations have been calculated from the LCV curves solving Eq. 7.4 numerically, and the trap concentrations have been obtained subtracting the carrier concentrations before and after photoionization of the given trap (Table 7.1). The largest error that results from the choice of C_{ins} appears in the trap with the highest $\Delta C/C_0$, i.e., trap T2 in the high N concentration sample (if C_{ins} was doubled the T2 concentration would decrease by a factor of 2). It is important to note that in some cases for low photon energies the LCV shape does not correspond to that expected for an MIS diode, which is likely due to the frequency used for the measurements not being low enough to allow the formation of a stable inversion channel. [132] Thus, in these cases the carrier concentration cannot be extracted from the LCV, and the corresponding trap concentration cannot be quantified (traps T2 and T3 for the low N sample). Table 7.1 sums up the observed deep levels and their concentrations, obtained from the LCV measurements using the MIS model. The $\Delta C/C_0$ values measured from the SSPC spectra are also shown, in order to better understand the scaling of N_T with the N concentration in those cases where it cannot be derived from the LCV curves. It can be observed how both N_T and $\Delta C/C_0$ are reduced for all traps according to the exposure to the N gas flow, which is consistent with a scaled N incorporation in the samples.

7.4.1 The N-related $E_V+0.47$ eV level

The deepest of the observed deep levels, the T3 level at $E_V + 0.47$ eV, could be related to the HT5 hole trap at $E_V + 0.48$ eV recently reported by Muret et al. in MBE-grown ZnO doped with N. [97] In their work, this hole trap is found to be related to N, and it is identified as an acceptor because of its large capture cross section. However, taking

7.4. TRAP CONCENTRATIONS BY LIGHTED CV PROFILING: THE MIS EFFECT

Table 7.1: Trap energies and concentrations (N_T) obtained from the SSPC and LCV analysis, using a MIS model (where available) for $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O:N}$. $\Delta C/C_0$ obtained from the SSPC spectra is also shown to allow comparison where N_T is not available.

Trap	$E_T - E_V$ (eV)	High N		Mid N		Low N	
		$\Delta C/C_0$	N_T (cm^{-3})	$\Delta C/C_0$	N_T (cm^{-3})	$\Delta C/C_0$	N_T (cm^{-3})
T1	0.16	-	-	9.5	5.45×10^{17}	1.85	2.06×10^{17}
T2	0.35	61.5	8.9×10^{18}	0.43	2.0×10^{16}	0.20	—
T3	0.47	0.17	5.8×10^{16}	0.04	6.0×10^{15}	0.01	—

into account the error bar, our T3 level observed here could also be related to the HT7 hole trap found by the same group at $E_V + 0.50 \text{ eV}$, which even though it has a large concentration, presents a low capture cross section and is not identified as a potential acceptor level.

7.4.2 The N-related $E_V + 0.35 \text{ eV}$ level

The T2 ($E_V + 0.35 \text{ eV}$) and T1 levels ($E_V + 0.16 \text{ eV}$) present very large concentrations that dominate the change in capacitance and that clearly scale with the N concentration. Whether N is incorporated in a substitutional site, or forms defect complexes, cannot be deduced from our analysis. However, the T2 energy level is not far from the deep acceptor N_O for which the calculated activation energy for the $\epsilon(0/-)$ charge state transition is located at $\sim 400 \text{ meV}$ above the VB in ZnO or at $\sim 468 \text{ meV}$ in $\text{Zn}_{0.75}\text{Mg}_{0.25}\text{O}$ [32, 78]. However, more recent calculations show that N is indeed a deep acceptor, further than 1 eV from the VBM, as was developed in chapter 1 [11, 86]. This defect is far from the band edge, and cannot be responsible by itself for the weak p-type conductivity sometimes observed by other groups. However, it is clear that at high concentrations it plays an important role in the capacitance variation in the high N devices, and in the trapping of the free charge.

7.4.3 The shallow $E_V + 0.16 \text{ eV}$ level

The T1 level ($E_V + 0.16 \text{ eV}$) cannot be observed in the high N sample, although it is responsible for the majority of the total $\Delta C/C_0$ variation in the mid N and low N samples. Because of its low activation energy, together with its prominence, it is a prime suspect as an efficient acceptor level in $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$. Indeed, it is possible that this level is contributing with holes to the inversion charge at the insulator/MgZnO interface, charge that produces the previously mentioned increase in $\Delta C/C_0$ in the mid N and low N for above bandgap illumination (Fig. 7.4-right). Since there is band bending close to the interface, the hole quasi-Fermi level may be close enough to the VB to allow the $E_V + 0.16 \text{ eV}$ acceptors to contribute to hole generation. This trap matches quite well that observed by Reynolds *et al.* [119] at $E_V + 0.13 \text{ eV}$ in ZnO grown by organometallic vapor phase epitaxy (OMVPE), which has been identified as a $\text{N}_\text{O}-\text{V}_{\text{Zn}}-\text{H}$ complex. Muret *et al.* [97] also observed a hole trap at $E_V + 0.19 \text{ eV}$ in MBE-grown ZnO, close to our T1 trap. Indeed, a theoretical calculation by Liu *et al.* [78] has shown

that a potential efficient acceptor in ZnO:N is the N_O-V_{Zn} complex, which introduces a level at $E_V + 0.16\text{ eV}$, also matching the energy of T2. A level with the same energy has been measured by Stehr *et al.* [129] by optically detected magnetic resonance in bulk ZnO implanted with N under different conditions. Finally, it is interesting to note that deep levels that are believed to arise from the V_{Zn} , reported at $\sim E_V + 0.28\text{ eV}$ and $E_V + 0.58\text{ eV}$ in both MBE and MOCVD MgZnO [37, 45, 138], have not been observed here, which could suggest that the V_{Zn} have been partially used up to form other defect complexes, like the N_O-V_{Zn} complex.

7.5 The effect of N implantation on MgZnO

This section¹ intends to analyze samples grown by MOCVD, similar to the ones shown in the previous sections. However, instead of introducing the N dopant during growth, these samples were implanted with N species as an alternative path to achieve p-type doping.

7.5.1 Available samples

A complete set of samples with increasing Mg content were provided by the group of Prof. Temmyo from Shizuoka University in Japan, grown by MOCVD in the a-plane orientation and 750 nm-thick. Among them, two samples were chosen for this deep level characterization: a reference ZnO layer, and another one with 9% Mg composition, because of its similarity with the samples previously measured and shown in this chapter. Each sample was cut in two pieces, with one of them being implanted with N by Dr. Andrés Redondo at the *Laboratorio de Física Nuclear* in Lisbon, Portugal. The implantation dose was chosen to be $1 \times 10^{15}\text{ cm}^{-2}$, with an acceleration energy of 150 keV . This was calculated so that N was introduced in the middle of the layer. The implanted samples were then annealed using a rapid thermal annealing (RTA) system for 120 s at 100°C and a temperature ramp of 45°C/s , in a N_2 environment at 1 bar pressure. This annealing process changed the brownish color the samples acquired following the implantation back to the natural transparent from ZnO.

7.5.2 Basic electrical characterization

Schottky diodes were processed on the four samples (ZnO and MgZnO, implanted and as-grown) using the procedure described in chapter 2. For simplicity, they will be labeled as ZnO-a, ZnO-imp, MgZnO-a and MgZnO-imp, where a- states for *as grown* and imp- for *implanted* (with the RTA annealing). Basic electrical characterization was performed on both samples, with a great inhomogeneity in the IV profiles. However, from CV profiles, the carrier concentrations were less sensitive to the differences between diodes and therefore a comparison between the samples could be performed, as shown in fig. 7.5.

The first and obvious result is that N implantation does not directly enhance compensation. Both as grown samples show a similar residual carrier concentration, about $1 - 2 \times 10^{17}\text{ cm}^{-3}$ for the ZnO sample and $2 - 3 \times 10^{17}\text{ cm}^{-3}$ for the MgZnO one. However, for the ZnO sample, after implantation and annealing, the carrier concentration increases to around $2 - 3 \times 10^{17}\text{ cm}^{-3}$. This slight increase can occur due to

¹This section has a lot to thank to Leonard Gura, who helped with the DLOS measurements and samples characterization during his visit to the ISOM laboratories during the academic year 2013/2014.

Figure 7.5: Net carrier concentration profiles for the as grown and implanted samples.

a reduction in compensating defects without N introducing any further compensation. The opposite happens in the MgZnO layer, where after the implantation+RTA process the carrier concentration is reduced down to $1 - 2 \times 10^{17} \text{ cm}^{-3}$. Despite all these shifts being subtle, the fact that the direction is opposite indicates that N is not playing a relevant role on the carrier concentration on these samples.

7.5.3 Characterization of implanted samples by DLOS

Fig. 7.6 summarizes the DLOS results for these samples. The first and most obvious result is that the implanted samples do not show any new level compared with the as grown versions. This is consistent with the CV measurements shown in fig. 7.5, where no appreciable difference was found. However, for the MgZnO sample a small shift in the bandgap energy obtained by DLOS was observed, of $\sim 40 \text{ meV}$. We believe this to be a real effect of the implantation+RTA process and not an MIS-like effect similar to the one described for the previous samples. The reason to believe this comes from the ΔC change upon illumination, that does not rise so drastically close to bandgap, discarding thus the presence of an inversion layer that will make the capacitance values to rise dramatically. Two possible reasons could explain this difference in bandgap energies. The first one is that each piece of the sample has indeed slightly different Mg compositions, due to inhomogeneities during the growth. The second one, less likely, could come from the thermal treatment performed after the implantation, which can act also activating residual Mg onto the lattice, or changing the strain conditions of the layer. Since no PL nor absorption measurement was carried out prior to the implantation+RTA treatment, it is very difficult to find the exact origin for this difference.

As for the defects observed in the DLOS measurements, the three defects previously mentioned were observed at $E_V + 0.72/0.78 \text{ eV}$, $E_V + 0.53/0.56 \text{ eV}$ and $E_V + 0.26/0.3 \text{ eV}$, with slight differences in the energy positions between the samples. However, all the three defects match quite well their energy positions and relative concentrations. Table 7.2 summarizes these results, indicating in the last row also the net carrier concentration obtained from the CV profiles.

For the case of the ZnO sample, it can be clearly observed how the trap density

Figure 7.6: SSPC spectra for both samples, as grown and implanted.

 Table 7.2: Summary of the concentration for the different levels observed by DLOS in the implanted (N_T^{imp}) and as grown (N_T^a) samples.

Level eV	ZnO		MgZnO	
	N_T^a (cm^{-3})	N_T^{imp} (cm^{-3})	N_T^a (cm^{-3})	N_T^{imp} (cm^{-3})
$E_V + 0.26/0.3$	3×10^{16}	4×10^{16}	7×10^{16}	6×10^{16}
$E_V + 0.53/0.56$	2×10^{15}	2×10^{15}	2×10^{15}	2×10^{15}
$E_V + 0.72/0.78$	2×10^{15}	2×10^{15}	5×10^{15}	4×10^{15}
deeper	—	1×10^{15}	4×10^{15}	6×10^{15}
N_{total}^{VB}	3.4×10^{16}	4.5×10^{16}	8×10^{16}	8×10^{16}
$N_D^+ - N_A^-$	$1 - 2 \times 10^{17}$	$2 - 3 \times 10^{17}$	$2 - 3 \times 10^{17}$	$1 - 2 \times 10^{17}$

correlates with the residual doping, both because of the increased concentration of the shallowest defect and an appreciable emission of deep levels close to the mid-gap region. This fact indicates that concurrent with the increased trap density close to the VB, a similar increase of the defects close to the CB must exist.

The MgZnO sample shows an almost equal number of defects close to the VB, with the same energy distribution. Therefore, the difference in the net carrier concentration must come from some reduction in the donor defects during the implantation and annealing processes. As for the origin of these defects, the two shallower ones are related with the V_{Zn} , which is consistently observed in ZnO and MgZnO materials, regardless of the growth method, as has been presented in the other chapters dedicated to DLOS in this thesis. No clear attribution is made for the deepest level, although a similar one was observed in undoped MBE material, described in chapter 5.

7.6 Conclusions

In summary, by means of the combination of DLOS and LCV, three levels close to the VB have been observed at $E_V + 0.16 eV$, $E_V + 0.35 eV$ and $E_V + 0.47 eV$ in $Zn_{0.9}Mg_{0.1}O$

grown in the presence of a N flow. The two traps closest to the VB may be assigned to N-related levels, and due to their large concentrations and low activation energy the $E_V + 0.16\text{ eV}$ may behave as an acceptor level and responsible for an increasing in the carrier compensation. The capacitance rose largely close to and above bandgap energies, which could only be explained invoking an MIS model. The LCV shapes at low frequency resembled those from an MIS under weak inversion, with the minimum capacitance allowing to compute the net carrier concentration for a given illumination energy. This allowed for the calculation of the defect concentration, which perfectly matched the N-concentration, making indeed the samples highly resistive.

Two ZnO and MgZnO samples were implanted with N, and DLOS was performed in order to measure the influence of N when not added during growth. Three main defects at $E_V + 0.72/0.78\text{ eV}$, $E_V + 0.53/0.56\text{ eV}$ and $E_V + 0.26/0.3\text{ eV}$ were measured, being the two shallowest ones attributed to the V_{Zn} , although no clear difference nor indication of N-related levels was obtained for the implanted samples. No MIS-like effect was observed for these devices, despite having been processed using the same H_2O_2 treatment, probably because of the lack of compensating acceptors.

The difference in the trap distribution between the N-doped samples during growth and the implanted series indicates that N plays an important role not only creating new defects, but reduces the appearing of the intrinsic ones observed in undoped material. This could help the design of more effective co-doping techniques that could lead to reliable p-type doping in ZnO.

Chapter 8

Deep level analysis of ZnO heterostructures

This section is based on the work carried out during the research visit performed to the Ohio State University during fall, 2014.

8.1 Introduction: 2DEG

During all the previous chapters, focus has been placed on thick layers, with the samples being composed of a single layer of material on top of a substrate. On them, deep level spectroscopy and other characterization techniques were performed, in order to assess the quality of the material and identify possible doping and defect issues. However, because of the lack of p-type doping, only unipolar devices can be reliably obtained. High electron mobility transistors (HEMT) are one of these devices, commonly used in radio-frequency circuits and high-power electronics. Using ZnO/MgZnO, there have been some reports on successful HEMTs [28, 51, 60, 64, 139].

These devices are based on the triangular potential well created in the conduction band, because of band offsets between two or more materials (in this case, ZnO and MgZnO), where a very small part of the CB can lay below the Fermi level. All the available electrons in the vicinity will fall into this well and create a two-dimensional electron gas (2DEG). Inside this layer, no impurity scattering processes occur, thus allowing for a high mobility. Therefore, the switching operation and the current flow in these kind of devices is largely enhanced.

Very good material is needed for the fabrication of successful HEMT structures, with nearly perfect interfaces and a precise control of the doping levels, layer thicknesses and strain. As it has been already mentioned in the previous chapters, this has almost only been attained by MBE growth in non-polar orientations, mainly m-plane (chapter 5). Although it has not been the purpose of this thesis, MgZnO has benefited from this advancements, too, and its quality, both grown as single layers and inside heterostructures, is remarkable [18, 134].

Two samples were provided by the group from Dr. Chauveau at CRHEA-CNRS in France, intended for the study of HEMT-like structures. A cross-section schematic can be observed in fig. 8.1, with the structures labeled as *simple* and *complex*. Both structures are similar, with the complex one adding a channel layer, intended as the region where the 2DEG would be formed, and a thicker MgZnO layer as a barrier. However, as it will be shown later, none of them indicated the presence of this 2DEG layer. The thin n-d ZnO

Figure 8.1: Schematic of the structure for the HEMT samples used in this study. The dashed line shows the relative position of the depletion region at room temperature.

layer on the surface has proved helpful to reduce leakage and improve the rectification behavior of the processed devices, something difficult with highly doped layers. The MgZnO had a nominal Mg composition of $\sim 30\%$, which makes their bandgap to be 3.6 eV . The Ga-doped layers had a nominal Ga concentration around $1 \times 10^{18}\text{ cm}^{-3}$.

Basic electrical characterization

The same Schottky diodes used during the previous chapters were processed on these samples, obtaining good rectification behavior, as shown in fig. 8.2, with over five orders of magnitude rectification ratio between $\pm 1\text{ V}$ in both samples. Considering the impossibility to get Schottky diodes in Ga-doped material, it is indeed an indication of the viability of the thin nid ZnO layer.

Measuring CV profiles (fig. 8.2) shows a net carrier concentration of about $7 \times 10^{16}\text{ cm}^{-3}$ for the complex structure and a bit higher, around $9 \times 10^{16}\text{ cm}^{-3}$ for the simple one. However, their measured depletion depths (assuming a homogeneous dielectric constant along the structure) is calculated to be about $\sim 200\text{ }\mu\text{m}$ for the simple structure, and deeper at $\sim 275\text{ }\mu\text{m}$ for the complex one. This finding indicates that the depletion region at room temperature and in the dark lays entirely in the buffer layer just above the substrate. Therefore, there is no 2DEG layer, which would have made the CV profile to stick to a constant capacitance despite the biasing (at least for some voltage region).

Moreover, the depletion edge is so clearly inside the buffer layer that during DLTS scans no contribution from the MgZnO layers will be observed. For the case of DLOS, the opposite can be stated, since it probes the entire depletion region, being able to excite defects present in any of the layers and interfaces present in the structures.

8.2 Deep level optical spectroscopy of heterostructures

As it was mentioned earlier in this chapter, DLOS was also performed on these structures, in order to characterize the defects present in the lower half of the bandgap. DLOS will be sensitive not only to the defects existing in the layer where the depletion edge lays, but to all the interfaces and different materials found in the structure.

8.2. DEEP LEVEL OPTICAL SPECTROSCOPY OF HETEROSTRUCTURES

Figure 8.2: Left: IV profiles for the simple and complex structures. Right: net doping profiles for both samples.

Being the defect concentration measured in terms of volume, unless an interface defect is present in such a high concentration that it can counter-act the interface bidimensional nature, it will not generate a trap signature that could be effectively observed. However, this levels will add up to the surface and minor defects creating an increase in photocapacitance without clear onsets.

Yet, the most important difficulty that arises from the measurement of deep levels in heterostructures comes from the difference in bandgaps and an intimate issue of the technique itself: the onsets must be referenced to the bandgap. Since in heterostructures there are, at least, two distinct values for this bandgap, distinction between the source and clear energy position of any onset is very difficult.

Figure 8.3 helps clarify this issue. On the left hand side, the overall spectra for both samples can be observed. Many onsets, both positive and negative are shown. However, their exact position with respect to the bandgap and the layer where they come from is doubtful. As it can be observed, a near bandgap rise in capacitance is obtained, similar to those shown for the simple structures from earlier chapters, only this rise happening twice, one time for each material. It can be seen that a certain scale in this onset magnitude exist proportional to the relative volume of MgZnO present in each sample.

On the right hand side of fig. 8.3, both bandgaps are positioned, with their difference in energy ~ 230 meV. Lower in energy, two positive onsets with a small fall in capacitance appear in the spectra, separated ~ 220 meV. Does this show the same defect in both materials happening at different illumination energies just because of the band-offset? Or is this the signature of two actual different defects in one of the layers? If so, which one of them is responsible for the deep level emission? Many similar questions can be formulated when analyzing this spectra, and no clear information can be obtained.

However, if thick layers for both materials are available, with similar growth conditions, it is possible that by comparison of the obtained levels, an assignment could be made. This "experience-based" assignments are risky, and can only indicate the presence of very well-known defects, and help clarify if their presence is enhanced, lowered or untouched from the shift from simple single layers to complex heterostructures.

As for the defects observed, applying this experience-based assignments, two levels could be clearly observed, at $E_V + 0.71$ eV, $E_V + 2.73$ eV and $E_V + 0.13$ eV. All of

Figure 8.3: Left: SSPC spectra of the two samples showing both bandgap values. Right: Detail for the trap double appearance when measuring heterostructures, measured without filter nor grating changes for the energy range shown. Y-axis is shown as $\Delta C/C_0$ since no N_D information can be used for complex structures.

them could be observed in both samples. The deepest one, at $E_V + 0.71 \text{ eV}$ could only be measured in both materials for the complex sample. However, this does not mean that the MgZnO layers in that sample do not show this defect. A feature repeated 220 meV higher in energy is observed for the complex structure, which when referencing to the MgZnO sample bandgap, yields the same energetic position as for pure ZnO. This, combined with the similarity both in energy and ΔC with previous measurements (chapter 5), makes us believe to be the same defect in both kind of materials.

The same can be stated for the shallow $E_V + 0.13 \text{ eV}$, which is responsible for nearly all of the capacitance rise in the SSPC spectra. This level is similar to one previously observed in ZnO:N (chapter 6) in behavior close to the VB and energy position. Independently of the sample, this level can be measured for both materials, considering the onset positions, separation and reference to the bandgap.

It is interesting to mention that for these samples, the commonly observed V_{Zn} signatures are not found at $\sim E_V + 0.25 \text{ eV}$ and $\sim E_V + 0.48 \text{ eV}$. This suggest that the growth conditions used for these samples, modified to allow for high-quality heterostructures, reduces the appearance of this defect.

A last defect, which can be referenced to the CB, or to the VB considering the trapping of minority carriers, is found at $E_V + 2.73 \text{ eV}$. The reason it has been referenced to the VB is that minority carrier trapping is unlikely to happen in unipolar material, where no holes are available. Moreover, it is discarded to come from a measurement feature since this negative onset appears "doubled" only in the complex structure, as will be expected from the increased volume of MgZnO material found in that sample. A similar behavior was already found when measuring using bias pulses along with optical pulses during DLOS scans (chapter 6). However, in this study there is no full depletion of the layers, nor it was observed a dependence with fill pulse conditions. Therefore, a reference to the defect being close to the CB is maintained.

Figure 8.4: DLTS spectra for both structures, for a RW of 80 s^{-1} , measured at $V_{bias} : -0.5\text{ V}$, $V_{fill} : 0\text{ V}$, $t_{fill} : 50\text{ ms}$.

8.3 DLTS levels measured in heterostructures

As it was explained in chapter 2, DLTS probes the traps that are found at the depletion layer edge, or at a Debye length from it. Thus, for the case of the samples under question in this study, only the defects present in the buffer layer below the heterostructures will be measured.

Figure 8.4 shows the measured spectra for both samples at the same reverse bias and rate window. As it can be directly observed, not only the trap concentration is lower for the complex structure, the number of levels observed is also lower. Figure 8.5 summarizes these findings, with table 8.1 showing all the parameters for all the defects observed by DLTS.

Only two defects are found in both samples, not surprisingly, the ones also observed in homoepitaxial ZnO (chapter 5): the E2 level at $E_C - 100\text{ meV}$ and the E3 level at $E_C - 300\text{ meV}$. For both samples the E3 level is dominant, despite the lowered trap density for the complex structure. Although these samples are m-plane, this behavior resembles that of r-plane material, as shown in chapter 5.

As for the defects not present in all samples, there is a high discrepancy between both samples. In the complex one, only one defect is observed at $E_C - 500\text{ meV}$, which is clearly not present in the simple structure. This defect, with a capture cross section of $\sim 2 - 6 \times 10^{-15}\text{ cm}^2$ is very similar to the E4 level reported by Auret *et al* [8] and the ET4 by Muret *et al* [97]. Albeit it being found to be a native (intrinsic) defect in ZnO, it was not found in the homoepitaxial layers from chapter 5 nor in the simple structure.

Four more different signatures are found in the simple structure, with activation energies of $E_C - 170\text{ meV}$, $E_C - 530\text{ meV}$, $E_C - 650\text{ meV}$ and $E_C - 920\text{ meV}$. The shallowest one does not show any parallelism with none of the previously observed defects. Therefore, its origin is completely unclear. Moreover, because of the close proximity from the larger E2 emission, very few data points can be added to the Arrhenius plot

Figure 8.5: Arrhenius plot for the DLTS spectra shown in fig. 8.4. The data points for the levels obtained by Muret *et al* [97] are also added for comparison.

(fig. 8.5), having a large error bar in the calculated parameters. However, regardless of this uncertainty, when plotting these data points together with the digitized Arrhenius plots from the literature, no proximity can be observed to any reported defect.

This is not the case for the three deeper defects observed in this simple structure. The defect with an activation energy of $E_C - 530 \text{ meV}$ shows a clear resemblance with the E4 level reported by Auret *et al* [8] which was analyzed in chapter 1. Similarly, the defect at $E_C - 650 \text{ meV}$ makes a very close match with the ET5 level published by Muret *et al* [97] and the $E_C - 920 \text{ meV}$ with their ET6 defect.

8.4 Conclusions: Valuable tips for measuring heterostructures

In this chapter two ZnO/MgZnO heterostructures have been characterized, initially with the aim of showing a 2DEG layer. Despite not having found it, deep level spectroscopy was performed on the samples, obtaining several defects and valuable knowledge about the measurement differences and limitations:

Basic electrical measurements. The first limitation comes from the basic electrical characterization, where the depletion edge can lay in any of the layers, depending on their doping, and their dielectric constant. A CV profile will yield a value for the capacitance, but translating it to a depth in the material, and subsequently to a net carrier concentration will be difficult if the dielectric constants are not equal. Moreover, if during the voltage sweep the depletion edge crosses an interface, because of the Debye length limitations [58], an uncertainty on the obtained values

8.4. CONCLUSIONS: VALUABLE TIPS FOR MEASURING HETEROSTRUCTURES

Table 8.1: Summary of the deep levels obtained from DLTS measurements in Zn/MgZnO heterostructures.

E_a (meV)	σ_n (cm ²)	N_T^{simple} (cm ⁻³)	$N_T^{complex}$ (cm ⁻³)
E2: $E_C - 100$	$1 - 4 \times 10^{-18}$	1×10^{14}	3×10^{14}
$E_C - 170$	$\sim 5 \times 10^{-16}$	5×10^{13}	–
E3: $E_C - 300$	$\sim 5 \times 10^{-16}$	5×10^{14}	2×10^{15}
ET4: $E_C - 500$	$\sim 2 \times 10^{-15}$	–	2×10^{14}
$E_C - 530$	$\sim 1 \times 10^{-12}$	2×10^{14}	–
ET5: $E_C - 650$	$\sim 3 \times 10^{-13}$	1×10^{14}	–
ET6: $E_C - 920$	$\sim 5 \times 10^{-13}$	1×10^{13}	–

both for concentration and depth will be added.

Optical measurements As it has been previously mentioned, during optical measurements, the probe photons will have to cross along all the depletion width where they can be absorbed. Therefore, defects present in any of the layers can contribute to the measured overall spectra. In order to assign correct energy positions to any feature, careful observance to duplicities and previous knowledge must be applied.

From the spectroscopic techniques, close to the VB various defects were found. A deep level at $E_V + 0.71$ eV was observed for both materials, and resembles that one previously observed in homoepitaxial m-ZnO. A donor-like level, from a negative onset at $E_V + 2.73$ eV was also observed. Finally, a shallow acceptor-like level at $E_V + 0.13$ eV was also found, measured in both materials, and responsible for most of the capacitance change close to the VB.

As for the results from DLTS, many levels were found in the upper part of the bandgap. Only two levels were clearly present in both samples: the previously reported E2 and E3 levels (more information about them can be found in chapter 1). The rest of the deep level emissions were distinct between the samples, without a clear indication as for the origin of these defects, and the reason why they are not observed equally in both samples, being the depletion region edge consistently measured to lay entirely in the buffer layer regardless of temperature and sample.

Part IV

Conclusions and future work

Chapter 9

Conclusions and future work

9.1 Conclusions

These last paragraphs of the document will now summarize the principal findings that have been obtained during the thesis. As it has been developed throughout the previous chapters, two main blocks have defined the work: techniques and experimental development, and ZnO/MgZnO characterization, focusing on the origin of the compensation by N-doping and intrinsic defects.

The MOCVD samples were obtained from the group of Prof. J. Temmyo from Schizuoka University in Japan, while the MBE-grown ones come from the group led by Dr. J.M. Chauveau at CRHEA-CNRS in France. During this thesis, two research visits were carried out, one in the group from Prof. S. Ringel at Ohio State University in the United States, where the ZnO/MgZnO heterostructures were analyzed by DLOS/DLTS and were described in chapter 8. The second one was carried out at CRHEA-CNRS with Dr. J.M. Chauveau, learning the details about MBE growth and structural characterization.

9.1.1 Undoped ZnO layers

As a first step towards analyzing doped material, three non intentionally doped ZnO samples were analyzed, grown by MBE in non-polar (m- and a-planes) and semipolar r-plane, in order to quantify the effect that the growth orientation plays on the residual carrier concentration. Schottky diodes were processed in all samples, obtaining good rectification properties that allowed to measure net carrier concentrations of $\sim 2 \times 10^{16} \text{ cm}^{-3}$ for the m-plane sample and $\sim 9 \times 10^{16} \text{ cm}^{-3}$ for the a- and r-planes.

PL measurements in these layers showed that at RT both non-polar orientations had a peak centered at a donor-bound exciton with a donor energy of only 25 meV . This effect was not observed for the r-plane sample, which has its near bandgap emission centered at another DX but without reaching the FX energy. The defect band observed at lower energies is similar for the non-polar orientations, centered around 2.45 eV , whereas for the r-plane material it is found at a lower energy, of about 2.3 eV . At LT, the FX emission can be clearly observed among the three orientations, indicating a good crystalline quality. The DX region is differently distributed, with different sharp and intense peaks. Peaks that can be assigned to phonon replicas, and an emission usually attributed to stacking faults, have been observed, although these SFs have not been obtained by structural measurements.

Figure 9.1: Summary bandstructure showing the different defects observed for the homoepitaxial ZnO grown in different orientations. Note: energies are not to scale.

From DLTS measurements, several defects were obtained, as can be observed in the upper part of fig. 9.1. Two of them are usually measured in ZnO, regardless of the growth method: the E2 and E3 levels, at energies of $E_C - 100 \text{ meV}$ and $E_C - 300 \text{ meV}$, respectively. While the shallower of these levels is dominant in the non-polar orientations, the E3 defect is responsible for almost all of the DLTS emission in the r-plane diodes. This E3 level has been related to the presence of H, which can easily diffuse in the material after growth. A very shallow defect, which perfectly matches the DX emission from PL is obtained in the non-polar (m- and a-planes) samples, with concentrations in the order of the E2 level. This defect has also been related to H. However, its low capture cross section could make it inefficient as a donor. A deeper level at $E_C - 585 \text{ meV}$ is only obtained for the r-plane layer, with a very low trap concentration, related to the V_O defect.

By DLOS (lower half in fig. 9.1) all samples look fairly similar, with three defects at $E_V + 0.25 \text{ eV}$, $E_V + 0.54 \text{ eV}$ and $E_V + 0.79 \text{ eV}$, being the shallowest one responsible for almost all of the capacitance change close to the VB, with concentrations of $\sim 2 \times 10^{16} \text{ cm}^{-3}$ for the m-plane and $\sim 2 \times 10^{17} \text{ cm}^{-3}$ for the a- and r-planes. All these levels have been also observed in previous studies from our group. The $E_V + 0.25 \text{ eV}$ and $E_V + 0.54 \text{ eV}$ levels are related to the V_{Zn} defect in its two charge states. The defect density at energies further from the VB that could not be resolved is not negligible, and accounts for over 10 % of the total capacitance change for all the layers.

Table 9.1: Summary of the total concentration of traps close to the CB, VB, and the residual carrier concentration obtained from CV measurements. Repetition of table 5.3 for clarity.

	m-plane	r-plane	a-plane
$N_{total}^{CB} (\text{cm}^{-3})$	1×10^{15}	5×10^{15}	1×10^{16}
$N_{total}^{VB} (\text{cm}^{-3})$	3×10^{16}	2×10^{17}	2×10^{17}
$N_D^+ - N_A^- (\text{cm}^{-3})$	2×10^{16}	9×10^{16}	9×10^{16}
$N_{total}^{CB} - N_{total}^{VB} (\text{cm}^{-3})$	2×10^{16}	$\sim 2 \times 10^{17}$	$\sim 2 \times 10^{17}$

As it can be observed in table 9.1, the total trap density close to the CB (N_{total}^{CB}) and the VB (N_{total}^{VB}) correlates with the net carrier concentration from CV measurements. Therefore, it can be stated that the reduction in net carrier concentration in the m-plane sample with respect to the a- and r-planes is coming from a reduction in the overall trap concentration, indicating an improved crystalline quality. This discards an increase in sample compensation, pointing m-plane material as more suitable for devices that need high quality material.

Among these devices, HEMTs are good candidates for unipolar devices, which do not need p-type doping, being ZnO/MgZnO a suitable system, because of the large offset in the CB that can be achieved with little stress on the structure. During the research visit to Ohio State University with Prof. Ringel, two ZnO/MgZnO samples, designed to check for the presence of a 2DEG layer, were analyzed by basic electrical characterization and DLOS/DLTS. Although no indication of the 2DEG was observed, the spectroscopic techniques yielded some defects already measured in ZnO and MgZnO, along with general tips for the measurement of complex material structures.

9.1.2 The effect of N-doping

Two studies were dedicated to the analysis of the role N-doping places in ZnO grown by MBE and MgZnO grown by MOCVD. Nitrogen was introduced during growth for the MBE and one of the MOCVD sets, whereas it was implanted and annealed for another MOCVD-grown set of samples. No p-type conductivity was obtained, although a strong compensation by acceptors resulting from N incorporation was observed and analyzed (fig. 9.2).

Homoepitaxial ZnO:N

Homoepitaxial ZnO has shown a low residual carrier concentration, which could help the shift towards p-type conductivity. Therefore, a series of N-doped MBE samples were grown by Dr. J.M. Chauveau at CRHEA-CNRS. From optical measurements, they showed very good crystalline quality in the undoped and lightly N-doped samples, whereas when increasing the N concentration, the optical properties of the material degraded. The commonly observed N-related DAP was measured at an energy of 3.234 eV, along with its phononic replicas, consistently with previous results that were summarized in chapter 1.

Schottky diodes were processed, obtaining good enough rectification behavior, with the sample ideality factor degrading as the N incorporation is increased. Similarly, the R_S value is also higher the larger the N concentration, ranging from only $0.4 \Omega \cdot cm^2$ in the undoped sample to $1.1 \times 10^3 \Omega \cdot cm^2$ for the sample with the larger N concentration. This is consistent with the reduction in net carrier density obtained by CV profiling, which goes down from $\sim 1 \times 10^{16} cm^{-3}$ in the undoped layer to $\sim 2 \times 10^{15} cm^{-3}$ in the lowest N-doped sample. Indeed, at 1 MHz, the N-doped samples look depleted, whereas when reducing the probing frequency, the referred fivefold reduction in doping density for the low N sample is obtained. The mid N sample could only be measured upon photoexcitation, and the high N one remained completely depleted even with illumination being applied.

The DLOS results are summarized in fig. 9.2, with only one defect being observed in the undoped and low N samples, at $E_V + 0.25 eV$, and that is responsible for almost all of the capacitance change close to bandgap. Indeed, these samples could not be measured

Figure 9.2: Schematic bandstructure for the defects observed in the lower part of the bandgap for the homoepitaxial MBE-grown ZnO and the MOCVD-grown Zn(Mg)O films doped and implanted with N. The levels are represented with their relative positions from the VB maximum, but without a scale. Note that the CB is also not at scale for clarity reasons.

up to the bandgap energies, due to the increased conductivity when reaching the excitonic absorption. For the mid N sample, along with the previously mentioned defect, three more onsets are found: a deeper one at $E_V + 0.48 \text{ eV}$ and two shallower defects at $E_V + 0.17 \text{ eV}$ and $E_V + 0.12 \text{ eV}$. The latter was responsible for all the capacitance change in this sample up to the bandgap energy. Interestingly, the $E_V + 0.17 \text{ eV}$ onset was negative, and only observed when applying an electrical fill pulse during the optical dark pulse. Therefore, this defect can be assigned to a minority carrier (hole) trap, since this sample is completely depleted in the dark, indicating the presence of a certain amount of holes in the material. Moreover, several studies have set the acceptor responsible for the DAP emission observed in LT-PL measurements to have an energy very close to this defect. Again, the two defects at $E_V + 0.25 \text{ eV}$ and $E_V + 0.48 \text{ eV}$ can be assigned to the two charge states of the V_{Zn} intrinsic defect.

MOCVD-grown MgZnO:N

For the case of the MOCVD-grown MgZnO:N samples (mid schematic in fig. 9.2), PL measurements were also performed, which helped to assess the MgZnO bandgap of $\sim 3.42 \text{ eV}$, with a much lower crystalline quality and no excitonic emission clearly observed. The processed Schottky diodes showed good rectification properties with leakage currents low enough to perform capacitance measurements, which had to be performed at low frequencies due to the samples compensation. Because of the insulating layer that appears due to the H_2O_2 treatment, the samples behaved as leaky MIS devices, thus making CV measurements unreliable for the obtention of net carrier concentration.

The first result coming from photocapacitance measurements was the correlation between the ΔC variation with the N concentration, indicating the presence of N-related acceptors. Three main trap energies were obtained at $E_V + 0.16 \text{ eV}$, $E_V + 0.35 \text{ eV}$ and $E_V + 0.47 \text{ eV}$, being the shallowest responsible for almost all of the capacitance rise close to the VB, although it could not be observed in the largely N-exposed sample. The energy for this level is consistent with the acceptor commonly observed in N-doped material, independent of the growth method, and which has been assigned to a complex defect involving N and some intrinsic point defect. The $E_V + 0.47 \text{ eV}$ onset has also been observed in other materials, and is possibly related to the V_{Zn} intrinsic defect.

Moreover, the observance of the shallow level, which probably involves this point defect, and not its first transition state, suggest that some of it could be combined with N to create this shallow acceptor.

The rising of the measured capacitance above bandgap energy illumination can only be explained invoking an MIS model, since PL measurements show that all samples have the same bandgap. Since $\Delta C/C_0 > 1$ for most traps, LCV was applied, obtaining CV profiles that resemble those ones from MIS devices in the inversion regime at intermediate frequencies, as explained during the first part of this thesis. From the C_{min} value measured in these LCV profiles, the trap concentration for each defect was obtained. Moreover, all these defects concentrations perfectly correlate with the N concentration, suggesting a N-related origin or dependence.

When analyzing the implanted MOCVD-grown Zn(Mg)O samples, two sets were processed, one of pure ZnO and another with a nominal Mg composition of 10%, which rose its bandgap up to 3.54 eV. For each sample, one piece was kept as-grown, while the other one was implanted with N and then annealed to activate the implanted impurities. From CV profiling it was observed that this N implantation did not compensate the material, with net carrier concentration values in the range of $1 - 3 \times 10^{17} \text{ cm}^{-3}$ independently of the Mg composition or implantation status.

By DLOS, three defects were measured at $E_V + 0.26/0.3 \text{ eV}$, $E_V + 0.53/0.56 \text{ eV}$ and $E_V + 0.72/0.78 \text{ eV}$, both in the as-grown and implanted samples. The variations in the energy positions come from the uncertainty in the correct bandgap for the MgZnO layers. No difference was observed between the samples nor due to the implantation. The two shallowest defects correspond again to the V_{Zn} signature. Therefore, it is shown that these processes did not create measurable change close to the VB.

Overall effect of N-doping

From a general point of view, it has been proved that introducing N during the growth largely affects the trap distribution of the material. Fig. 9.2 summarizes all the levels observed in the studies with N-doped samples. Several defects have been observed coming from the introduction of N, being the most significant one measured both for MBE and MOCVD material at an energy around $E_V + 0.16/0.17 \text{ eV}$, and which perfectly matches the acceptor commonly observed by different techniques in N-doped material, and responsible for the DAP emission in LT-PL.

Other levels that have been consistently observed are those arising from the V_{Zn} intrinsic defect, with one charge state occurring around $E_V + 0.25 - 0.3 \text{ eV}$ and another one at $E_V + 0.47 - 0.6 \text{ eV}$. This defect was also observed in the non intentionally doped homoepitaxial layers, and was responsible for the majority of the capacitance change in them.

In the MBE ZnO:N a shallow defect at $E_V + 0.12 \text{ eV}$ was measured, which is responsible for the steep rise in capacitance in the medium N-doped layer. However, it could not be observed in any of the other N-doping studies, being its origin unclear. One deeper defect was observed during the implantation study at $E_V + 0.72 - 0.78 \text{ eV}$, which was also measured in the different orientations study. Since the growth method was different, an intrinsic defect is suggested, although no clear assignment can be made.

9.1.3 Deep level spectroscopies of MIS structures

As it was described in the previous sections, the necessary H_2O_2 treatment in ZnO can induce a thin insulating layer that creates an MIS device. However, no proper model to measure deep level spectroscopy techniques was available. It was directly obvious that extending these capacitance-based techniques to these devices could help measure highly doped samples and materials that suffer from surface accumulation layers, etc.

Firstly, the dynamic operation and electrical equivalent circuit of an MIS device were analyzed in the depletion regime, which is the only one suitable for these techniques, as it exposes the material beneath the surface. Under steady state operation, the main consideration comes from the voltage drop between the different layers, with the percentage of that voltage being proportional to the relative magnitude between the insulator and depletion capacitances. Therefore, the thicker the insulator, the more voltage will drop in this layer, minimizing the biasing range that can be applied to the semiconductor.

However, the main contribution from the developed model comes under transient operation, basic in any capacitance-based deep level spectroscopic technique. From basic electrical theory, any capacitor needs some time to charge or discharge. Therefore, after applying an square pulse, a voltage transient will appear in the insulator capacitance, making thus the voltage drop in the semiconductor behave also as a transient, in comparison with the immediate shift that is assumed for the depletion region. If this voltage transient is introduced into the expression for the total capacitance considering also the emission coming from deep levels, a complex expression is obtained, in which two regimes can be separated: an insulator-dominated and a depletion-dominated regime.

Under the insulator-dominated regime, the overall capacitance transient that will be measured using the equipment, the emission from deep levels will be faster than the capacitance response to the voltage transient, which will mask any signal coming from the defect emission. In the depletion-dominated regime, the time constant for the insulator capacitor is very small (fast), so the voltage can be assumed to change instantly after the fill pulse. This is the regime in which ideally an MIS device will be operated for the purpose of deep level spectroscopic techniques.

Indeed, by performing simulations under these regimes, it can be observed that in an insulator-dominated regime, there is no effect of the deep level signatures in the DLTS spectra. However, in the depletion-dominated situation, DLTS peaks will be obtained, only with a reduced amplitude when compared with the non-MIS devices. The factor in which these peaks are reduced can be calculated using another expression, called the *correctivity factor* (α), which depends solely on the depletion capacitance under steady state conditions, and the insulator capacitance. The most direct result is that there is no need to know the exact value of the latter as long as it is much higher than the depletion capacitance, making $\alpha \approx 1$. Under this condition, the defect concentration values obtained by DLTS can be calculated using the same expressions than for non-MIS devices, albeit there existing an insulating layer.

Since MIS structures can be useful to characterize highly doped material, in which Schottky contacts are difficult to process, two test devices were processed, one undoped and a Ga-doped one, using the standard H_2O_2 treatment that has shown to create a thin insulating layer. This was assessed by performing a low-frequency lighted CV profile at an illumination energy close to bandgap, which helps create enough holes to drive the device into a weak inversion layer. When performing DLTS scans in this samples, the E3 level was clearly observed, with nearly the same concentration and capture cross section for both materials. Despite the presence of the insulator, a well-known level was observed

in an undoped layer, and a highly-doped material, with a net carrier concentration in the $1 \times 10^{18} \text{ cm}^{-3}$ range was effectively measured, thus validating the model.

9.1.4 Equipment improvements and development

During the realization of this PhD thesis, an important effort has been placed not only in the purely scientific research, but on optimizing and developing the techniques and measurement setups that were used to characterize the materials. This development can be divided onto hardware and software modifications, with the latter affecting almost all the techniques, where the former are focused on the capacitance-based techniques. Additionally, a new foto-lithography mask was designed to improve the use of the available material, normally scarce, and to add a contact pad that allows to perform bonding on semitransparent devices. This mask allowed to have more diodes available in a smaller piece of material.

From the hardware point of view, the first improvement was the design and implementation of a low-noise transimpedance amplifier, which allows to convert the current AC signal to a voltage one that can be fed into the lock-in amplifier for low frequency capacitance measurements. Not only the noise levels are lower, but the gain can be controlled, in order to further amplify small signals, or even attenuate large ones compared with the existing current input in the lock-in instrument. Another improvement was the inclusion of an advanced centering box for the capacitance measurements at 1 MHz, which allows to control the offset value at very small increments, keeping the transients centered in smaller scales of the measurement equipment, improving the sensitivity.

In order to further improve the overall sensitivity of the capacitance measurements both using the capacitance meter and the lock-in amplifier, an advanced DAQ solution was implemented, with much larger sampling rates than the existing DSOs, and with a larger digital resolution. This, combined with some filtering and oversampling techniques allowed to largely increase the sensitivity of the CV/DLTS/DLOS measurements.

The last hardware inclusion was a custom-made box that allows to properly control the operation of the high-power Xe lamp used for experiments with UV illumination, plus the optical shutters, from the computer. By doing so, the number of hours the lamp is on can be substantially reduced. Additionally, the water filter temperature is monitored, allowing to turn of the lamp if a certain threshold is reached. These box was designed as part of a Final Degree project by the student A. Gómez Hernández.

On the software side, most of the improvements were dedicated to increase the efficiency of the systems. Some techniques require the repetition of a certain step many times, making a single second improvement on these steps timing to generate a large reduction in the overall scan duration. The data saving process was improved so at each step the values are written onto disk, minimizing the chance of data lost. By improving the DLTS program, the system now obtains more RWs, with a larger resolution, and performs both double-boxcar and Fourier analysis in real time, creating a large amount of data. Analysis software was developed to assist the obtention of computed parameters from the measurement data. This routines were programmed not only for the *complex* techniques such as DLOS/DLTS, but also for the basic electrical characterization (CV and IV). Lastly, general software optimizations were carried out, modernizing the internal structure of the programs to be more stable, readable and upgradeable, along with reworked user interfaces that simplify the configuration and are more result-driven.

9.2 Future work

After many years, despite the great advancements achieved during the thesis, several studies can be suggested for future students, which continue with the existing knowledge and further improve the knowledge of ZnO and related materials, as well as the deep level spectroscopic techniques.

9.2.1 Ga-doping in ZnO

Since p-type doping has been unsuccessful, in order to process unipolar devices, the control of the n-type doping is crucial, and the understanding of the trap generation as a result of doping is key to fully explain the behavior of the doped material. Among the many dopants proposed that were described during the introduction chapters, Ga has been one of the most promising, and indeed the growth group at CRHEA-CNRS has proved to be able to control its incorporation onto ZnO. Although a first series of doped samples were received during this thesis, the doping levels were far too high (above $1 \times 10^{19} \text{ cm}^{-3}$) to allow for DLTS or DLOS analysis. To carry out this study, it would be interesting to analyze the impact of Ga doping from low values, i.e. $5 \times 10^{16} \text{ cm}^{-3}$, up to high values of $8 \times 10^{18} \text{ cm}^{-3}$, in order to maintain the depletion region within measurable limits. Additionally, a thin undoped ZnO top layer can help the processing of Schottky diodes on these highly doped samples.

9.2.2 Residual carrier concentration: undoped samples

Additionally to the understanding of the donors introduced intentionally, the sometimes large net carrier concentration that undoped samples show must be further analyzed. During this thesis, it was shown that m-plane has a lower carrier concentration, not because of compensation, but from an overall reduction in defect density.

As a next step, the effect of growth conditions, which has shown in preliminary results to reduce the net carrier concentration down to $\sim 5 \times 10^{14} \text{ cm}^{-3}$, must be similarly analyzed, obtaining the total trap density close to both bands, and analyzing whether this reduction comes from compensation, an improved crystalline quality, or because of the effect of single defects appearing or disappearing from the material. A set of samples is already under processing for DLOS/DLTS measurement, in order to continue with this study.

9.2.3 Depth-resolved measurements: constant capacitance

Not only the measurement in bulk material is interesting, but the depth distribution of these levels in the sample is also important. For example, some defects can come from the diffusion of impurities from the substrate or from the surface. However, due to the sometimes large changes in depletion width with temperature or illumination energy, it is very difficult to correlate the obtained spectra with their relative depth.

Constant capacitance measurements can thus be carried out, maintaining the capacitance value constant, and measuring the voltage (both steady state and transient) that must be applied to obtain such condition. Therefore, the depletion width will be homogeneous throughout the measurement, and by performing scans at different capacitance values, the depth profile for single defects can be obtained.

However, the equipment for these kind of measurements is not easy to implement. High speed digitization and processing must be performed in order to obtain a controller

that is able to maintain the capacitance value constant by rapidly responding to any change due to illumination, temperature, and generally, emission from the deep levels. Since these process are fast, and devices respond instantly to any change in biasing, delay on the controller is also crucial. Even though computers are getting faster, nowadays the only option to perform these kind of controllers is by designing custom ASICs, or using high-performance FPGAs, which need to include auxiliary electronics to adapt the signals and impedances to the already existing measurement equipment.

9.2.4 ZnO/MgZnO heterostructures

If at any point the previously mentioned depth-resolved capacitance measurements are implemented, it would be important to analyze the interfaces between ZnO and MgZnO used in heterostructures. A set of samples with only one interface and two thick ZnO and MgZnO layers have been designed, which allow to maintain the depletion region slightly below the interface, above it, or to control the position by biasing to lie in any of the materials. By doing so, the complexities of most powerful heterostructures are reduced, and the influence of the multilayer growth can be measured in a controlled way, avoiding part of the difficulties observed during the study of the HEMT-like heterostructures during this thesis.

9.2.5 Setup improvements

Generally, both hardware and software can be further improved in order to increase the capacities of the system, being the most important ones, as far as the author's experience is concerned:

Cryostat modification The cryostat that has been used during this thesis is limited to 330 K as its upper limit, which is sometimes not enough to characterize deep levels in the material. Therefore, the limit of ~ 1 eV usually set for DLTS measurements cannot be achieved. Since the temperature controller can be easily replaced in the software, and the cryostat itself is not a crucial part of the setup, as long as holders are available, a substitution with another model could increase the temperature range in which the system can operate.

Lock-in amplifier The current lock-in amplifier is several decades old, and limited to 100 kHz. Thus, the range between 100 kHz and 1 MHz is not available for measurement, although it could be interesting for lightly compensated samples, in which the higher frequency is not suitable, but without largely compromising the SNR. Additionally, modern solutions can measure up to several MHz, which could allow to fully substitute both lock-in amplifier and capacitance meter, creating a simpler and more homogeneous setup.

Software optimizations Many options can be added in the software suite that controls the measurement. Besides working on the modernization of the code already performed, features such as real-time error logging and operator notifications in case of mis-functioning, can be implemented. From the measurement point of view, Laplace DLTS can also be added, since it has proved to be able to discriminate between levels very close in energy, in order to further improve the capabilities of the DLTS system.

Appendices

Appendix A

ZnO deep levels tables

Deep levels obtained during this thesis

From DLPS measurements

Energy (meV)	$N_T cm^{-3}$	Material	Assignment
$E_V + 120$	1×10^{15}	m-ZnO:N (mid N)	N-induced (SFs?)
$E_V + 130$	–	ZnO/ZnMgO simple het.	–
	–	ZnO/ZnMgO complex het.	–
$E_V + 160$	–	ZnMgO:N (high N)	N-related
	5×10^{17}	ZnMgO:N (mid N)	N-related
	2×10^{17}	ZnMgO:N (low N)	N-related
$E_V + 170$	–	m-ZnO:N (mid N)	N-related (DAP)
$E_V + 250$	1×10^{16}	m-ZnO:N (low N)	$V_{Zn} [\epsilon(0, -)]$
$E_V + 250$	2×10^{16}	m-ZnO nid	$V_{Zn} [\epsilon(0, -)]$
$E_V + 250$	2×10^{17}	a-,r-ZnO nid	$V_{Zn} [\epsilon(0, -)]$
$E_V + 260 - 300$	3×10^{16}	ZnO nid	$V_{Zn} [\epsilon(0, -)]$
	4×10^{16}	ZnO:N (imp)	$V_{Zn} [\epsilon(0, -)]$
	7×10^{16}	ZnMgO nid	$V_{Zn} [\epsilon(0, -)]$
	6×10^{16}	ZnMgO:N (imp)	$V_{Zn} [\epsilon(0, -)]$
$E_V + 350$	9×10^{18}	ZnMgO:N (high N)	N-related
	2×10^{16}	ZnMgO:N (mid N)	N-related
	–	ZnMgO:N (low N)	N-related
$E_V + 470$	6×10^{16}	ZnMgO:N (high N)	N-related
	6×10^{15}	ZnMgO:N (mid N)	N-related
	–	ZnMgO:N (low N)	N-related

APPENDIX A. ZNO DEEP LEVELS TABLES

$E_V + 480$	1×10^{14}	m-ZnO:N (mid N)	N-related
$E_V + 540$	$3 - 5 \times 10^{15}$	a-,r-ZnO nid	$V_{Zn} [\epsilon(-, 2-)]$
$E_V + 530 - 560$	2×10^{15}	ZnO nid	$V_{Zn} [\epsilon(-, 2-)]$
	2×10^{15}	ZnO:N (imp)	$V_{Zn} [\epsilon(-, 2-)]$
	2×10^{15}	ZnMgO nid	$V_{Zn} [\epsilon(-, 2-)]$
	2×10^{15}	ZnMgO:N (imp)	$V_{Zn} [\epsilon(-, 2-)]$
$E_V + 580$	5×10^{14}	m-ZnO nid	$V_{Zn} [\epsilon(-, 2-)]$
$E_V + 710$	–	ZnO/ZnMgO simple het.	–
	–	ZnO/ZnMgO complex het.	–
$E_V + 720 - 780$	2×10^{15}	ZnO nid	–
	2×10^{15}	ZnO:N (imp)	–
	5×10^{15}	ZnMgO nid	–
	4×10^{15}	ZnMgO:N (imp)	–
$E_V + 790$	2×10^{14}	m-ZnO nid	–
$E_V + 790$	$1 - 3 \times 10^{15}$	a-,r-ZnO nid	–
$E_V + 2.73 \text{ eV}$	–	ZnO/ZnMgO simple het.	–
	–	ZnO/ZnMgO complex het.	–

From DLTS measurements

Label	E_a (meV)	σ_n (cm ²)	N_T (cm ⁻³)	Material	Assignment
–	$E_C - 25$	9×10^{-21}	$2 - 3 \times 10^{15}$	m-,a-ZnO nid	H?, DX
E2	$E_C - 100$	5×10^{-18}	$< 1 \times 10^{14}$	r-ZnO nid	–
	$E_C - 100$	7×10^{-18}	1×10^{15}	m-ZnO nid	–
	$E_C - 100$	8×10^{-18}	5×10^{15}	a-ZnO nid	–
E2	$E_C - 100$	$1 - 4 \times 10^{-18}$	$1 - 3 \times 10^{14}$	ZnO/ZnMgO het.	–
–	$E_C - 170$	5×10^{-16}	5×10^{13}	ZnO/ZnMgO-sh het.	X
E3	$E_C - 300$	5×10^{-16}	5×10^{14}	m-ZnO nid	H-related
	$E_C - 300$	5×10^{-16}	2×10^{15}	a-ZnO nid	H-related
	$E_C - 300$	6×10^{-16}	5×10^{15}	r-ZnO nid	H-related
E3	$E_C - 300$	5×10^{-16}	5×10^{14}	ZnO/ZnMgO-sh	H-related
E3	$E_C - 300$	5×10^{-16}	2×10^{15}	ZnO/ZnMgO-ch	H-related
ET4	$E_C - 500$	2×10^{-15}	2×10^{14}	ZnO/ZnMgO-ch	–
–	$E_C - 530$	1×10^{-12}	2×10^{14}	ZnO/ZnMgO-sh	–
E4	$E_C - 585$	7×10^{-13}	2×10^{15}	r-ZnO nid	V_O
ET5	$E_C - 650$	3×10^{-13}	1×10^{14}	ZnO/ZnMgO-sh	V_O
ET5	$E_C - 920$	5×10^{-13}	1×10^{13}	ZnO/ZnMgO-sh	–

Deep levels previously reported in the literature

Note: Since this section summarizes defect signatures obtained from many different characterization techniques and from material grown by various methods, the energy positions will be given referenced when existing, or as absolute emission energy. The Aux. field will include any other parameter considered relevant (as concentration, capture cross section, etc for DLTS/DLOS measurements). Since several reviews exist for the different peaks obtained in PL measurements, only the relevant ones will be referenced (i.e. that ones assigned to a defect, dopant, etc). Ordered by reference number (alphabetically in the Bibliography section.).

Note: HT=hydrothermal; SCVT: Seeded Chemical Vapor Transport; MOVPE: Metalorganic Vapor Phase Epitaxy; MG: Melt-Grown; OMVPE: Organometallic vapor phase epitaxy

Label	Energy	Aux.	Material	Origin	Technique	Ref.
E ₃₁	$E_C - 31 \text{ meV}$	–	ZnO	–	DLTS	[7]
E ₆₄	$E_C - 64 \text{ meV}$	–	ZnO	–	DLTS	[7]
E ₁₄₀	$E_C - 140 \text{ meV}$	–	ZnO	–	DLTS	[7]
E ₂₈₀	$E_C - 280 \text{ meV}$	–	ZnO	–	DLTS	[7]
E3:E ₃₀₀	$E_C - 300 \text{ meV}$	$\sigma = 2 \times 10^{-16}$	ZnO	–	DLTS	[7]
E3':E ₃₇₀	$E_C - 370 \text{ meV}$	$\sigma = 7 \times 10^{-15}$	ZnO	extended	DLTS	[7]
E1	$E_C - 0.12 \text{ eV}$	–	SCVT,MG ZnO	X	DLTS	[8]
E3	$E_C - 0.29 \text{ eV}$	–	SCVT,MG ZnO	X	DLTS	[8]
–	$E_D = 16.1 \text{ meV}$	–	MG ZnO	Zn_i	TDH	[13]
–	$E_D = 22 \text{ meV}$	–	MG ZnO N+ imp	Zn_i	TDH	[13]
–	$E_D = 50.8 \text{ meV}$	–	MG ZnO	Zn_i	TDH	[13]

E1	$E_t = 120 \text{ meV}$	–	MG ZnO imp	–	DLTS	[13]
E3	$E_t = 310 \text{ meV}$	–	MG ZnO	Zn_i	DLTS	[13]
E4	$E_t = 530 \text{ meV}$	–	MG ZnO	–	DLTS	[13]
E3	$E_C - 275 \text{ meV}$	$\sigma = 3 \times 10^{-16}$	MOVPE ZnO	dual defect	DLTS	[21]
–	$E_A = 135 \text{ meV}$	–	MBE ZnO:N	N-related	Hall effect	[22]
E3	$E_C - 0.27 \text{ eV}$	–	ZnO	–	DLTS	[29]
E4	$E_C - 0.49 \text{ eV}$	–	ZnO	–	DLTS	[29]
Es	$E_C - 0.49 \text{ eV}$	–	ZnO	surface	DLTS	[29]
E1	$E_V + 0.3 \text{ eV}$	–	MOCVD ZnMgO	V_{Zn}	DLOS	[37]
E2	$E_V + 0.6 \text{ eV}$	–	MOCVD ZnMgO	V_{Zn}	DLOS	[37]
E3	$E_C - 2.6 \text{ eV}$	–	MOCVD ZnMgO	Mg-related	DLOS	[37]
E4	$E_C - 2.1 \text{ eV}$	–	MOCVD ZnMgO	Mg-related	DLOS	[37]
E5	$E_C - 1.4 \text{ eV}$	–	MOCVD ZnMgO	Mg-related	DLOS	[37]
–	$E_V + 280 \text{ meV}$	–	MOCVD ZnMgO	V_{Zn}	DLOS	[45]
–	$E_V + 580 \text{ meV}$	–	MOCVD ZnMgO	V_{Zn}	DLOS	[45]
D1	$E_D = 35 \text{ meV}$	–	ZnO	H	Hall effect	[46]
D2	$E_D = 66 \text{ meV}$	–	ZnO	–	Hall effect	[46]

E3	$E_C - 300 \text{ meV}$	–	HT ZnO	H-related	DLTS	[48]
E4	$E_C - 570 \text{ meV}$	–	HT ZnO	V_O	DLTS	[49]
–	$E_D = 52 \text{ meV}$	–	ZnO	H	Raman+PL	[73]
–	$E_D = 35 \text{ meV}$	–	ZnO	H	Raman+PL	[73]
–	3.324 eV	Spot on SF	m-ZnO	Stacking Faults	LT-CL	[77]
–	3.316 eV	Far from SF	m-ZnO	Stacking Faults	LT-CL	[77]
–	3.315 eV	–	ZnO	N-related A^0X	PL	[81]
D1	$E_D = 37 \text{ meV}$	–	ZnO	–	Hall effect & PL	[83]
D2	$E_D = 67 \text{ meV}$	–	ZnO	–	Hall effect & PL	[83]
–	2.26 eV	–	ZnO powder	O_i -related	PL	[85]
–	2.35 eV	–	ZnO powder	V_{Zn}	PL	[85]
–	2.48 eV	–	ZnO powder	V_O	PL	[85]
–	$E_V + 3.21 \text{ eV}$	–	CVT ZnO:Cu	Cu	PL	[89]
–	$E_V + 1.4 \text{ eV}$	–	CVT ZnO:N	N_O	PL	[89]
–	$E_V + 0.86 \text{ eV}$	–	CVT ZnO:Li	Li	PL	[89]
–	$E_D = 46.1 \text{ meV}$	–	ZnO	H	PL	[90]
–	$E_D = 51.55 \text{ meV}$	–	ZnO	Al	PL	[90]

–	$E_D = 53 \text{ meV}$	–	ZnO	–	PL	[90]
–	$E_D = 54.6 \text{ meV}$	–	ZnO	Ga	PL	[90]
–	$E_D = 63.2 \text{ meV}$	–	ZnO	In	PL	[90]
–	$E_D = 72.6 \text{ meV}$	–	ZnO	–	PL	[90]
E1	$E_C - 120 \text{ meV}$	$\sigma \approx 5 \times 10^{-12}$ $N_T \approx 5 \times 10^{14}$	ZnO	O-rich	DLTS	[95]
E2	$E_C - 100 \text{ meV}$	–	ZnO	–	DLTS	[95]
E3	$E_C - 300 \text{ meV}$	$\sigma \approx 1 \times 10^{-16}$ $N_T \approx 1 \times 10^{16}$	ZnO	–	DLTS	[95]
E4	$E_C - 600 - 670 \text{ meV}$	–	ZnO	–	DLTS	[95]
E1	$E_C - 0.12 \text{ eV}$	–	ZnO	–	DLTS	[96]
E2	$E_C - 0.10 \text{ eV}$	–	ZnO	–	DLTS	[96]
E3	$E_C - 0.30 \text{ eV}$	–	ZnO	–	DLTS	[96]
ET1	$E_C - 186 \text{ meV}$	$\sigma = 1 \times 10^{-17}$ $N_T = 1 \times 10^{15}$	MBE ZnO	–	DLTS	[97]
ET3	$E_C - 400 \text{ meV}$	$\sigma = 1 \times 10^{-14}$ $N_T = 1 \times 10^{15}$	MBE ZnO	–	DLTS	[97]
ET4	$E_C - 490 \text{ meV}$	$\sigma = 4 \times 10^{-15}$ $N_T = 1 \times 10^{16}$	MBE ZnO	–	DLTS	[97]

ET5	$E_C - 552 \text{ meV}$	$\sigma = 8 \times 10^{-15}$ $N_T = 3 \times 10^{16}$	MBE ZnO	–	DLTS	[97]
ET6	$E_C - 600 \text{ meV}$	$\sigma = 6 \times 10^{-16}$ $N_T = 1 \times 10^{16}$	MBE ZnO	–	DLTS	[97]
ET7	$E_C - 520 \text{ meV}$	$\sigma = 6 \times 10^{-18}$ $N_T = 1 \times 10^{16}$	MBE ZnO	–	DLTS	[97]
ET8	$E_C - 575 \text{ meV}$	$\sigma = 1 \times 10^{-17}$ $N_T = 1 \times 10^{16}$	MBE ZnO	–	DLTS	[97]
HT1	$E_V + 120 \text{ meV}$	$\sigma = 2 \times 10^{-18}$ $N_T = 8 \times 10^{15}$	MBE ZnO:N	N-related	DLTS	[97]
HT2	$E_V + 190 \text{ meV}$	$\sigma = 3 \times 10^{-15}$ $N_T = 8 \times 10^{15}$	MBE ZnO:N	N-related	DLTS	[97]
HT3	$E_V + 177 \text{ meV}$	$\sigma = 1 \times 10^{-18}$ $N_T = 2 \times 10^{16}$	MBE ZnO:N	N-related	DLTS	[97]
HT4	$E_V + 280 \text{ meV}$	$\sigma = 2 \times 10^{-16}$ $N_T = 2 \times 10^{16}$	MBE ZnO:N	–	DLTS	[97]
HT5	$E_V + 485 \text{ meV}$	$\sigma = 5 \times 10^{-14}$ $N_T = 2 \times 10^{16}$	MBE ZnO:N	N-related	DLTS	[97]
HT6	$E_V + 466 \text{ meV}$	$\sigma = 4 \times 10^{-16}$ $N_T = 2 \times 10^{16}$	MBE ZnO:N	N-related	DLTS	[97]
HT7	$E_V + 503 \text{ meV}$	$\sigma = 3 \times 10^{-17}$ $N_T = 3 \times 10^{16}$	MBE ZnO:N	N-related	DLTS	[97]

–	3.31 eV	–	ZnO:N	DAP	PL	[98]
–	3.334 eV	–	ZnO:N	A^0X	PL	[98]
E3	$E_T = 0.3$ eV	–	sputtering ZnMgO	–	admittance & DLTS	[113]
–	$E_A = 0.14$ eV	–	sputtering ZnMgO	–	optical DLTS	[113]
–	$E_A = 0.84$ eV	–	sputtering ZnMgO	–	optical DLTS	[113]
E2	$E_C - 0.18$ eV	$\sigma = 5 \times 10^{-17}$	HT ZnO	–	DLTS	[115]
E3	$E_C - 0.3$ eV	$\sigma = 1 \times 10^{-15}$	HT ZnO	–	DLTS	[115]
E4	$E_C - 0.54$ eV	$\sigma = 1 \times 10^{-13}$	HT ZnO	–	DLTS	[115]
E5	$E_C - 1.0$ eV	$\sigma = 8 \times 10^{-14}$	HT ZnO	polishing-related	DLTS	[115]
E6	$E_C - 1.2$ eV	$\sigma = 5 \times 10^{-15}$	HT ZnO	polishing-related	DLTS	[115]
E1a	$E_C - 0.10$ eV	$\sigma = 3 \times 10^{-15}$	HT ZnO	–	DLTS	[114]
E1b	$E_C - 0.11$ eV	$\sigma = 2 \times 10^{-17}$	HT ZnO	–	DLTS	[114]
E2	$E_C - 0.19$ eV	$\sigma = 6 \times 10^{-17}$	HT ZnO	impurity	DLTS	[114]
E3	$E_C - 0.30$ eV	$\sigma = 2 \times 10^{-15}$	HT ZnO	–	DLTS	[114]
E4	$E_C - 0.54$ eV	$\sigma = 1 \times 10^{-16}$	HT ZnO	V_O	DLTS	[114]
E5a	$E_C - 0.72$ eV	$\sigma = 1 \times 10^{-15}$	HT ZnO	–	DLTS	[114]
E5b	$E_C - 1.00$ eV	$\sigma = 2 \times 10^{-12}$	HT ZnO	–	DLTS	[114]

E2	$E_C - 190 \text{ meV}$	–	HT ZnO	Fe-related	DLTS	[116]
E3	$E_C - 300 \text{ meV}$	–	HT ZnO	Fe-related	DLTS	[116]
E4	$E_C - 540 \text{ meV}$	–	HT ZnO	intrinsic	DLTS	[116]
–	$E_D = 53 \text{ meV}$	–	MOVPE ZnO:Ga (imp)	Ga donor	magneto-PL	[118]
–	$E_A = 163 - 196 \text{ meV}$	–	MOVPE ZnO:N (imp)	N acceptor	PL	[118]
–	$E_A = 130 \text{ meV}$	–	OMVPE ZnO:N	$V_{Zn} - N_O - H^+$	PL	[119]
D1	$E_D = 30 \pm 10 \text{ meV}$	–	HT ZnO	H	TAS	[120]
D2	$E_D = 50 \pm 10 \text{ meV}$	–	HT ZnO	Al	TAS	[120]
Dx	$E_D = \sim 100 \text{ meV}$	–	HT ZnO	V_O	TAS	[120]
D3	$E_D = \sim 300 \text{ meV}$	–	HT ZnO	–	TAS	[120]
–	3.31 eV , $E_A = 130 \text{ meV}$	–	VPE ZnO	SF	PL	[121]
E1	$E_C - 98 \text{ meV}$	$\sigma = 4 \times 10^{-14}$ $N_T = 2 \times 10^{15}$	PLD ZnO	–	DLTS	[122]
E3	$E_C - 303 \text{ meV}$	$\sigma = 9 \times 10^{-16}$ $N_T = 5 \times 10^{15}$	PLD ZnO	–	DLTS	[122]
T4	$E_V + 1.6 \text{ eV}$	–	PLD ZnO		PhotoCap.	[122]
TH1	$E_V + 0.3 \text{ eV}$	–	PLD ZnO		PhotoCap.	[122]
TH2	$E_V + 0.430 \text{ eV}$	$\sigma = 5 \times 10^{-12}$	PLD ZnO		PhotoCap.	[122]

–	$E_A = 160$ meV	–	ZnO:N	–	PL	[129]
–	$E_A \approx 120$ meV	–	MBE ZnO	–	PL	[131]
–	3.26 eV	–	MBE ZnO	DAP	PL	[131]
–	3.31 eV	–	MBE ZnO	F,A	PL	[131]
–	$E_A = 160$ meV	–	MBE ZnO:N	–	PL	[135]
–	2.2	PL peak at 1.7 eV	SCVT ZnO	N_O	PL	[136]
–	$E_C - 23$ meV	$\sigma = 3 \times 10^{-17}$	HT ZnO	H	Q-DLTS	[137]
–	$E_C - 11$ meV	$\sigma = 4 \times 10^{-17}$	HT ZnO	strain	Q-DLTS & PL	[137]
DL1	$E_V + 2.0$ eV	–	MOVPE ZnO	V_O	PL	[138]
DL2	2.3 eV	–	MOVPE ZnO	$Mg_i/Zn_i - O_i$	PL	[138]
DL3	2.5 eV	–	MOVPE ZnO	$Mg_i/Zn_i - V_{Zn}$	PL	[138]
DL4	2.8 eV	–	MOVPE ZnO	V_{Zn}	PL	[138]
DL5	$E_V + 3.0$ eV	–	MOVPE ZnO	Zn_i	PL	[138]
E3	$E_C - 0.31$ eV	$\sigma = 5 \times 10^{-13}$	HT ZnO	–	DLTS	[140]
E4	$E_C - 0.58$ eV	$\sigma = 1 \times 10^{-16}$	HT ZnO	–	DLTS	[140]
E5	$E_C - 0.19$ eV	$\sigma = 1 \times 10^{-15}$	HT ZnO	–	DLTS	[140]
E3	$E_C - 300$ meV	–	ZnO	–	DLTS	[141]

E4	$E_C - 0.57$ eV	–	ZnO	–	DLTS	[141]
E5	$E_C - 1.06$ eV	–	ZnO	Intrinsic	DLTS	[141]
E6	$E_C - 1.2$ eV	–	ZnO	Interstitials	DLTS	[141]
E1	$E_C - 110$ meV	–	MG ZnO	–	DLTS	[145]
E3	$E_C - 310$ meV	–	MG ZnO	–	DLTS	[145]
E4	$E_C - 530$ meV	–	MG ZnO	–	DLTS	[145]
A2	$E_V + 150$ meV	–	MG ZnO	–	DLTS	[145]
A3	$E_V + 280$ meV	–	MG ZnO	Li_{Zn}	DLTS	[145]
I4	3.3628 eV, $E_D = 46.1$ meV	–	ZnO	–	PL	[146]
I6	3.3608 eV, $E_D = 51.5$ meV	–	ZnO	–	PL	[146]
I8	3.3598 eV, $E_D = 54.6$ meV	–	ZnO	–	PL	[146]
I9	3.3567 eV, $E_D = 63.2$ meV	–	ZnO	–	PL	[146]
I10	3.3531 eV, $E_D = 72.6$ meV	–	ZnO	–	PL	[146]
–	$E_A = 209$ meV	–	SCVT ZnO	N-related	PL	[148]

–	$E_D = 52 \text{ meV}$	–	ZnO	–	PL	[154]
–	$E_A = 165 \text{ meV}$	–	ZnO	–	PL	[154]
–	3.33 eV	–	ZnO	structural def.	PL	[154]

Appendix B

List of publications and conference participations

Publications as first author

- Kurtz, A., Hierro, A., Muñoz, E., Mohanta, S. K. & Nakamura, A. 2014. Acceptor levels in ZnMgO:N probed by deep level optical spectroscopy. *Applied Physics Letters*, 104. [66]
- Kurtz, A., Hierro, A., López-Ponce, M., Tabares, G. & Chauveau, J. M. 2016. Electrical mechanisms for carrier compensation in homoepitaxial nonpolar m-ZnO doped with nitrogen. *Semiconductor Science and Technology*, 31. [65]
- Kurtz, A., Muñoz, E., Chauveau, J. M. & Hierro, A. 2017. Deep-level spectroscopy in metal-insulator-semiconductor structures. **Journal of Physics D: Applied Physics**, 50, 065104 (9 pp.)-065104 (9 pp.). [67]

Publications as collaborator

- Hierro, A., Tabares, G., López-Ponce, M., Muñoz, E., Kurtz, A., Vinter, B. & Chauveau, J. M. 2015. ZnO/ZnMgO multiple quantum well light polarization sensitive photodetectors. In: Teherani, F. H., Look, D. C. & Rogers, D. J. (eds.) *Oxide-Based Materials and Devices VI*.
- López-Ponce, M., Hierro, A., Marin-Borras, V., Tabares, G., Kurtz, A., Albert, S., Agouram, S., Muñoz-Sanjose, V., Muñoz, E. & Ulloa, J. M. 2015. Optical properties of ZnMgO films grown by spray pyrolysis and their application to UV photodetection. *Semiconductor Science and Technology*, 30.
- Hierro, A., Tabares, G., López-Ponce, M., Ulloa, J. M., Kurtz, A., Muñoz, E., Marin-Borras, V., Muñoz-Sanjose, V. & Chauveau, J. M. 2016. ZnMgO-based UV photodiodes: a comparison of films grown by spray pyrolysis and MBE. *Proceedings of the SPIE*, 9749, 97490W (6 pp.)-97490W (6 pp.).
- Hierro, A., Tabares, G., López-Ponce, M., Ulloa, J. M., Kurtz, A., Muñoz, E., Marin-Borras, V., Muñoz-Sanjose, V. & Chauveau, J. M. 2016. ZnMgO-based UV photodiodes: a comparison of films grown by spray pyrolysis and MBE. In:

APPENDIX B. LIST OF PUBLICATIONS AND CONFERENCE PARTICIPATIONS

Teherani, F. H., Look, D. C. & Rogers, D. J. (eds.) *Oxide-Based Materials and Devices VII*.

- Nieda, Y., Suzuki, M., Nakamura, A., Temmyo, J., Tabares, G., Kurtz, A., LOPEZ, M., Ulloa, J. M., Hierro, A. & Muñoz, E. 2016. Wurtzite $\text{Zn}_{1-y}(\text{Mg}_x\text{Cd}_{1-x})_y\text{O}$ quaternary systems for photodiodes in visible spectral range. *Journal of Crystal Growth*, 449, 27-34.
- Huerta-Barbera, A., Guia, L. M., Klymov, O., Marin-Borras, V., Martinez-Tomas, C., Tamayo-Arriola, J., Kurtz, A., Montes-Bajo, M., Muñoz, E., Hierro, A. & Muñoz-Sanjose, V. 2016. MOCVD growth of CdO very thin films: Problems and ways of solution. *Applied Surface Science*, 385, 209-15.
- Utrilla, A. D., Reyes, D. F., Llorens, J. M., Artacho, I., Ben, T., González, D., Gazevic, Z., Kurtz, A., Guzman, A., Hierro, A. & Ulloa, J. M. 2017. Thin GaAsSb capping layers for improved performance of InAs/GaAs quantum dot solar cells. *Solar Energy Materials and Solar Cells*, 159, 282-289.

Conference participations as presenter

- A. Kurtz; G. Tabares; E. Muñoz; S. Kumar Mohanta; A. Hierro; A. Nakamura; J. Temmyo, "Acceptor Levels Probed by DLOS in ZnMgO:N ", International II-VI Conference, 9-13 Septiembre 2013
- A. Kurtz, A. Hierro, L. Gura, E. Muñoz, J.M. Chauveau, "Deep Level Analysis of Homoepitaxial ZnO Doped with N", MRS 2014 Fall meeting, Boston, EEUU, 30-Nov a 5-Dic de 2014
- A. Kurtz, "Deep Level Spectroscopy and its applications to Zn(Mg)O ", Ciclo de seminarios del CRHEA, Valbonne-Sophia Antipolis, Francia, 14-Dic-2015
- A. Kurtz, A. Hierro, E. Muñoz, "Deep level spectroscopy in metal-insulator-semiconductor structures", 13th EXMATEC - Expert Evaluation and Control of Compound Semiconductor Materials and Technologies, Aveiro (Portugal), 30/06/2016. Se obtuvo el premio "Sociedade Portuguesa de Física".
- A. Kurtz, E. Muñoz, J.M. Chauveau, A. Hierro "Deep level analysis of non-polar and semipolar homoepitaxial ZnO", 9th International Workshop on Zinc Oxide and Related Materials, Taipei (Taiwán), Noviembre de 2016.

Collaborations in conference papers

- A. Hierro, A. Kurtz, E. Muñoz, S.K. Mohanta, A. Nakamura, J. Temmyo "Deep and shallow traps in ZnMgO:N ", SPIE Photonics West, San Francisco, EEUU, Febrero 2014
- A. Hierro, A. Kurtz, L. Gura, E. Muñoz, and J.M. Chauveau, "Deep levels in homoepitaxial ZnO and the effect of N doping", 18th European-Molecular Beam Epitaxy Workshop, Canazei (Italy), 2015

-
- A. Hierro, G. Tabares, M. Lopez-Ponce, J.M. Ulloa, A. Kurtz, E. Muñoz, V. Marin-Borras, V Muñoz-SanJose, J.M. Chauveau, "ZnMgO-based UV photodiodes: a comparison of films grown by spray pyrolysis and MBE", SPIE Photonics West, San Francisco, EEUU, February 2016

Other merits

- Finalist in the XI business creation competition, UPM, Madrid, 2014-2015
- Certified Labview Associate Developer (CLAD), Serial Number: 100-316-11930; National Instruments, April 2016
- Certified Labview Developer (CLD), Serial Number: 100-916-10957; National Instruments, December 2016

Bibliography

- [1] Sadao Adachi. *Properties of semiconductor alloys: group-IV, III-V and II-VI semiconductors*, volume 28. John Wiley & Sons, 2009.
- [2] Vlasdimir I Anisimov, IV Solovyev, MA Korotin, MT Czyżyk, and GA Sawatzky. Density-functional theory and nio photoemission spectra. *Physical Review B*, 48(23):16929, dec 1993.
- [3] A. Armstrong, A. R. Arehart, and S. A. Ringel. A method to determine deep level profiles in highly compensated, wide band gap semiconductors. *Journal of Applied Physics*, 97(8):6, apr 2005.
- [4] ABM Almamun Ashrafi, Akio Ueta, Adrian Avramescu, Hidekazu Kumano, Ikuo Suemune, Young-Woo Ok, and Tae-Yeon Seong. Growth and characterization of hypothetical zinc-blende zno films on gaas (001) substrates with zns buffer layers. *Applied Physics Letters*, 76(5):550–552, jan 2000.
- [5] F. D. Aurret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, and D. C. Look. Electrical characterization of 1.8 mev proton-bombarded zno. *Applied Physics Letters*, 79(19):3074–3076, nov 2001.
- [6] F. D. Aurret, S. A. Goodman, M. J. Legodi, W. E. Meyer, and D. C. Look. Electrical characterization of vapor-phase-grown single-crystal zno. *Applied Physics Letters*, 80(8):1340–1342, feb 2002.
- [7] F. D. Aurret, W. E. Meyer, P. J. J. van Rensburg, M. Hayes, J. M. Nel, H. von Wenckstern, H. Schmidt, G. Biehne, H. Hochmuth, M. Lorenz, and M. Grundmann. Electronic properties of defects in pulsed-laser deposition grown zno with levels at 300 and 370 mev below the conduction band. *Physica B: Condensed Matter*, 401:378–381, dec 2007.
- [8] F. D. Aurret, J. M. Nel, M. Hayes, L. Wu, W. Wesch, and E. Wendler. Electrical characterization of growth-induced defects in bulk-grown zno. *Superlattices and Microstructures*, 39(1-4):17–23, jan 2006.
- [9] Vitaliy Avrutin, Donald J. Silversmith, and Hadis Morkoc. Doping asymmetry problem in zno: Current status and outlook. *Proceedings of the IEEE*, 98(7):1269–1280, jul 2010.
- [10] L. R. Bailey, T. D. Veal, P. D. C. King, C. F. McConville, J. Pereiro, J. Grandal, M. A. Sanchez-Garcia, E. Munoz, and E. Calleja. Band bending at the surfaces of in-rich ingan alloys. *Journal of Applied Physics*, 104(11):113716, dec 2008.

BIBLIOGRAPHY

- [11] J. Bang, Y. Y. Sun, D. West, B. K. Meyer, and S. B. Zhang. Molecular doping of zno by ammonia: a possible shallow acceptor. *J. Mater. Chem. C*, 3(2):339–344, 2015.
- [12] P. Blood and J.W. Orton. *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States*. Techniques of Physics. Academic Press, 1st edition, 1992.
- [13] G. Brauer, W. Anwand, W. Skorupa, J. Kuriplach, O. Melikhova, C. Moisson, H. von Wenckstern, H. Schmidt, M. Lorenz, and M. Grundmann. Defects in virgin and n+-implanted zno single crystals studied by positron annihilation, hall effect, and deep-level transient spectroscopy. *Physical Review B*, 74(4), jul 2006.
- [14] L. J. Brillson, Y. F. Dong, F. Tuomisto, B. G. Svensson, A. Y. Kuznetsov, D. Douthett, H. L. Mosbacker, G. Cantwell, J. Z. Zhang, J. J. Song, Z. Q. Fang, and D. C. Look. Interplay of native point defects with zno schottky barriers and doping. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*, 30(5):11, sep 2012.
- [15] L. J. Brillson and Y. C. Lu. Zno schottky barriers and ohmic contacts. 109(12):33.
- [16] A. Chantre, G. Vincent, and Dubois. Deep-level optical spectroscopy in gaas. *Physical Review B*, 23(10):5335–5359, may 1981.
- [17] J. M. Chauveau, C. Morhain, M. Teisseire, M. Lauegt, C. Deparis, J. Zuniga-Perez, and B. Vinter. (zn, mg)o/zno-based heterostructures grown by molecular beam epitaxy on sapphire: Polar vs. non-polar. *Microelectronics Journal*, 40(3):512–516, mar 2009.
- [18] J. M. Chauveau, M. Teisseire, H. Kim-Chauveau, C. Deparis, C. Morhain, and B. Vinter. Benefits of homoepitaxy on the properties of nonpolar (zn,mg)o/zno quantum wells on a-plane zno substrates. *Applied Physics Letters*, 97(8):081903, aug 2010.
- [19] J. M. Chauveau, M. Teisseire, H. Kim-Chauveau, C. Morhain, C. Deparis, and B. Vinter. Anisotropic strain effects on the photoluminescence emission from heteroepitaxial and homoepitaxial nonpolar (zn,mg)o/zno quantum wells. *Journal of Applied Physics*, 109(10):102420, may 2011.
- [20] Gauthier Chicot, Pierre Muret, Jean-Louis Santailier, Guy Feuillet, and Julien Pernot. Oxygen vacancy and ec- 1 ev electron trap in zno. *Journal of Physics D: Applied Physics*, 47(46):465103, oct 2014.
- [21] Gauthier Chicot, Julien Pernot, Jean-Louis Santailier, Céline Chevalier, Carole Granier, Pierre Ferret, Alexandre Ribeaud, Guy Feuillet, and Pierre Muret. Electronic properties of e3 electron trap in n-type zno. *physica status solidi (b)*, 251(1):206–210, sep 2013.
- [22] B. Claflin, D. C. Look, S. J. Park, and G. Cantwell. Persistent n-type photoconductivity in p-type zno. *Journal of Crystal Growth*, 287(1):16–22, jan 2006.
- [23] Chris G. Van de Walle. Hydrogen as a cause of doping in zinc oxide. *Physical Review Letters*, 85(5):1012–1015, jul 2000.

- [24] L. Dobaczewski, P. Kaczor, I. D. Hawkins, and A. R. Peaker. Laplace transform deep-level transient spectroscopic studies of defects in semiconductors. *Journal of Applied Physics*, 76(1):194–198, jul 1994.
- [25] Yufeng Dong, Z. . Q. Fang, D. C. Look, D. R. Doust, G. Cantwell, J. Zhang, J. J. Song, and Leonard J. Brillson. Defects at oxygen plasma cleaned zno polar surfaces. *Journal of Applied Physics*, 108(10):103718, nov 2010.
- [26] SM Evans, NC Giles, LE Halliburton, and LA Kappers. Further characterization of oxygen vacancies and zinc vacancies in electron-irradiated zno. *Journal of Applied Physics*, 103(4):043710, feb 2008.
- [27] Jerome Faist, Federico Capasso, Deborah L. Sivco, Carlo Sirtori, Albert L. Hutchinson, and Alfred Y. Cho. Quantum cascade laser. *Science*, 264(5158):553–556, apr 1994.
- [28] J Falson, Y Kozuka, JH Smet, T Arima, A Tsukazaki, and M Kawasaki. Electron scattering times in zno based polar heterostructures. *Applied Physics Letters*, 107(8):082102, aug 2015.
- [29] Z. Q. Fang, B. Claflin, D. C. Look, Y. F. Dong, H. L. Mosbacker, and L. J. Brillson. Surface traps in vapor-phase-grown bulk zno studied by deep level transient spectroscopy. *Journal of Applied Physics*, 104(6):063707, sep 2008.
- [30] Zhe Chuan Feng. *Handbook of Zinc Oxide and Related Materials: Volume one: Materials*, volume 2. CRC Press, 2012.
- [31] Sergio Franco. *Design with Operational Amplifiers and Analog Integrated Circuits*. McGraw-Hill, 2003.
- [32] Y. Q. Gai, B. Yao, Z. P. Wei, Y. F. Li, Y. M. Lu, D. Z. Shen, J. Y. Zhang, D. X. Zhao, X. W. Fan, Li Jingbo, and Xia Jian-Bai. Effect on nitrogen acceptor as mg is alloyed into zno. *Applied Physics Letters*, 92(6):062110–1–062110–062110–3, feb 2008.
- [33] N. Y. Garces, N. C. Giles, L. E. Halliburton, G. Cantwell, D. B. Eason, D. C. Reynolds, and D. C. Look. Production of nitrogen acceptors in zno by thermal annealing. *Applied Physics Letters*, 80(8):1334–1336, feb 2002.
- [34] N. Y. Garces, L. J. Wang, N. C. Giles, L. E. Halliburton, G. Cantwell, and D. B. Eason. Molecular nitrogen ($n_2(-)$) acceptors and isolated nitrogen (n^-) acceptors in zno crystals. *Journal of Applied Physics*, 94(1):519–524, jul 2003.
- [35] NY Garces, L Wang, L Bai, NC Giles, LE Halliburton, and G Cantwell. Role of copper in the green luminescence from zno crystals. *Applied Physics Letters*, 81(4):622–624, jul 2002.
- [36] Q. L. Gu, C. C. Ling, X. D. Chen, C. K. Cheng, A. M. C. Ng, C. D. Beling, S. Fung, A. B. Djuricic, L. W. Lu, G. Brauer, and H. C. Ong. Hydrogen peroxide treatment induced rectifying behavior of au/n-zno contact. *Applied Physics Letters*, 90(12):122101, mar 2007.

BIBLIOGRAPHY

- [37] E. Gur, G. Tabares, A. Arehart, J. M. Chauveau, A. Hierro, and S. A. Ringel. Deep levels in a-plane, high mg-content mgxzn1-xo epitaxial layers grown by molecular beam epitaxy. *Journal of Applied Physics*, 112(12):7, dec 2012.
- [38] Emre Gur, Gema Tabares, Aaron Arehart, Jean Michele Chauveau, Adrián Hierro, and Steve Ringel. High level of mg alloying effects on the deep level defects in mgxzn1-xo . In *AVS 58th International Symposium&Exhibition*.
- [39] RN Hall. Germanium rectifier characteristics. In *Physical Review*, volume 83, pages 228–228. AMERICAN PHYSICAL SOC ONE PHYSICS ELLIPSE, COLLEGE PK, MD 20740-3844 USA, 1951.
- [40] Y. W. Heo, Y. W. Kwon, Y. Li, S. J. Pearton, and D. P. Norton. p-type behavior in phosphorus-doped (zn,mg)o device structures. *Applied Physics Letters*, 84(18):3474–3476, may 2004.
- [41] YW Heo, DP Norton, and SJ Pearton. Origin of green luminescence in zno thin film grown by molecular-beam epitaxy. *Journal of Applied Physics*, 98(7):073502, oct 2005.
- [42] YW Heo, SJ Park, K Ip, SJ Pearton, and DP Norton. Transport properties of phosphorus-doped zno thin films. *Applied Physics Letters*, 83(6):1128–1130, aug 2003.
- [43] A. Hierro, A. R. Arehart, B. Heying, M. Hansen, J. S. Speck, U. K. Mishra, S. P. DenBaars, and S. A. Ringel. Capture kinetics of electron traps in mbe-grown n-gan. *physica status solidi (b)*, 228(1):309–313, nov 2001.
- [44] A. Hierro, S. A. Ringel, M. Hansen, J. S. Speck, U. K. Mishra, and S. P. DenBaars. Hydrogen passivation of deep levels in n-gan. *Applied Physics Letters*, 77(10):1499–1501, sep 2000.
- [45] A. Hierro, G. Tabares, J. M. Ulloa, E. Munoz, A. Nakamura, T. Hayashi, and J. Temmyo. Carrier compensation by deep levels in $\text{zn1-xmgxo/sapphire}$. *Applied Physics Letters*, 94(23):3, jun 2009.
- [46] Detlev M Hofmann, Albrecht Hofstaetter, Frank Leiter, Huijuan Zhou, Frank Henecker, Bruno K Meyer, Sergei B Orlinskii, Jan Schmidt, and Pavel G Baranov. Hydrogen: a relevant shallow donor in zinc oxide. *Physical Review Letters*, 88(4):045504, jan 2002.
- [47] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864, nov 1964.
- [48] A Hupfer, C Bhodoo, L Vines, and BG Svensson. The e_3 center in zinc oxide: Evidence for involvement of hydrogen. *Applied Physics Letters*, 104(9):092111, mar 2014.
- [49] A Hupfer, C Bhodoo, L Vines, and BG Svensson. Formation and annihilation of e_4 centers in zno: Influence of hydrogen. *Journal of Applied Physics*, 119(18):181506, may 2016.

-
- [50] K. Ikeda and H. Takaoka. Deep level fourier spectroscopy for determination of deep level parameters. *Japanese Journal of Applied Physics*, 21(3):462–466, mar 1982.
- [51] Y Imanaka. Cyclotron resonance in zno heterostructures at high magnetic fields. *Journal of Low Temperature Physics*, 170(5-6):389–396, oct 2013.
- [52] A. Janotti, E. Snow, and C. G. Van de Walle. A pathway to p-type wide-band-gap semiconductors. *Applied Physics Letters*, 95(17):3, oct 2009.
- [53] A. Janotti and C. G. Van de Walle. Fundamentals of zinc oxide as a semiconductor. *Reports on Progress in Physics*, 72(12):29, oct 2009.
- [54] Anderson Janotti, David Segev, and Chris G Van de Walle. Effects of cation d states on the structural and electronic properties of iii-nitride and ii-oxide wide-band-gap semiconductors. *Physical Review B*, 74(4):045202, jul 2006.
- [55] Anderson Janotti and Chris G Van de Walle. Hydrogen multicentre bonds. *Nature Materials*, 6(1):44–47, dec 2006.
- [56] Anderson Janotti and Chris G. Van de Walle. Native point defects in zno. *Physical Review B*, 76(16), oct 2007.
- [57] P. H. Jefferson, S. A. Hatfield, T. D. Veal, P. D. C. King, C. F. McConville, J. Zuniga-Perez, and V. Munoz-Sanjose. Bandgap and effective mass of epitaxial cadmium oxide. *Applied Physics Letters*, 92(2):022101, jan 2008.
- [58] W.C. Johnson and P.T. Panousis. The influence of debye length on the c-v measurement of doping profiles. *IEEE Transactions on Electron Devices*, 18(10):965–973, oct 1971.
- [59] R.J. Kaplar. *CHARACTERIZATION OF DEEP LEVEL DEFECTS IN InGaAsN*. PhD thesis.
- [60] DF Kärcher, AV Shchepetilnikov, Yu A Nefyodov, J Falson, IA Dmitriev, Y Kozuka, D Maryenko, A Tsukazaki, SI Dorozhkin, IV Kukushkin, et al. Observation of microwave induced resistance and photovoltage oscillations in mgzno/zno heterostructures. *Physical Review B*, 93(4):041410, jan 2016.
- [61] Y. Kashiwaba, T. Abe, A. Nakagawa, I. Niikura, M. Daibo, T. Fujiwara, and H. Osada. Formation of a zno₂ layer on the surface of single crystal zno substrates with oxygen atoms by hydrogen peroxide treatment. *Journal of Applied Physics*, 113(11):5, mar 2013.
- [62] A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle. First-principles study of native point defects in zno. *Physical Review B*, 61(22):15019–15027, jun 2000.
- [63] W Kohn and LJ Sham. Quantum density oscillations in an inhomogeneous electron gas. *Physical Review*, 137(6A):A1697, mar 1965.
- [64] VE Kozlov, AB Van'kov, SI Gubarev, IV Kukushkin, VV Solovyev, J Falson, D Maryenko, Y Kozuka, A Tsukazaki, M Kawasaki, et al. Microwave magnetoplasma resonances of two-dimensional electrons in mgzno/zno heterojunctions. *Physical Review B*, 91(8):085304, feb 2015.
-

BIBLIOGRAPHY

- [65] A. Kurtz, A. Hierro, M. Lopez-Ponce, G. Tabares, and J. M. Chauveau. Electrical mechanisms for carrier compensation in homoepitaxial nonpolar m-zno doped with nitrogen. *Semiconductor Science and Technology*, 31(3):035010, feb 2016.
- [66] A. Kurtz, A. Hierro, E. Munoz, S. K. Mohanta, and A. Nakamura. Acceptor levels in $\text{znmg}_{0.1}\text{n}$ probed by deep level optical spectroscopy. *Applied Physics Letters*, 104(8):081105, feb 2014.
- [67] A Kurtz, E Muñoz, J M Chauveau, and A Hierro. Deep-level spectroscopy in metal–insulator–semiconductor structures. *Journal of Physics D: Applied Physics*, 50(6):065104, jan 2017.
- [68] D. V. Lang. Deep-level transient spectroscopy: A new method to characterize traps in semiconductors. *Journal of Applied Physics*, 45(7):3023–3032, jul 1974.
- [69] David V. Lang. Recalling the origins of {DLTS}. *Physica B: Condensed Matter*, 401-402:7–9, dec 2007. Proceedings of the 24th International Conference on Defects in Semiconductors.
- [70] S. Lautenschlaeger, S. Eisermann, G. Haas, E. A. Zolnowski, M. N. Hofmann, A. Laufer, M. Pinnisch, B. K. Meyer, M. R. Wagner, J. S. Reparaz, G. Callsen, A. Hoffmann, A. Chernikov, S. Chatterjee, V. Bornwasser, and M. Koch. Optical signatures of nitrogen acceptors in zno. *Physical Review B*, 85(23):7, jun 2012.
- [71] S. Lautenschlaeger, S. Eisermann, B. K. Meyer, G. Callsen, M. R. Wagner, and A. Hoffmann. Nitrogen incorporation in homoepitaxial zno cvd epilayers. *physica status solidi (RRL) - Rapid Research Letters*, 3(1):16–18, jan 2009.
- [72] S. Lautenschlaeger, M. Hofmann, S. Eisermann, G. Haas, M. Pinnisch, A. Laufer, and B. K. Meyer. A model for acceptor doping in zno based on nitrogen pair formation. *physica status solidi (b)*, 248(5):1217–1221, feb 2011.
- [73] E.V. Lavrov. Hydrogen in zno. *Physica B: Condensed Matter*, 404(23):5075–5079, dec 2009.
- [74] W. J. Lee, J. Kang, and K. J. Chang. Defect properties and p-type doping efficiency in phosphorus-doped zno. *Physical Review B*, 73(2):024117, jan 2006.
- [75] Y. F. Li, B. Yao, Y. M. Lu, Z. P. Wei, Y. Q. Gai, C. J. Zheng, Z. Z. Zhang, B. H. Li, D. Z. Shen, X. W. Fan, and Z. K. Tang. Realization of p-type conduction in undoped $\text{mg}(x)\text{zn}(1-x)\text{o}$ thin films by controlling mg content. *Applied Physics Letters*, 91(23):3, dec 2007.
- [76] Al Liechtenstein, VI Anisimov, and J Zaanen. Density-functional theory and strong interactions: Orbital ordering in mott-hubbard insulators. *Physical Review B*, 52(8):R5467, aug 1995.
- [77] W. H. Lin, U. Jahn, H. T. Grahn, L. W. Chang, M. M. C. Chou, and J. J. Wu. Spectral and spatial luminescence distribution of m-plane zno epitaxial films containing stacking faults: A cathodoluminescence study. *Applied Physics Express*, 6(6):4, jun 2013.

- [78] Lei Liu, Jilian Xu, Dandan Wang, Mingming Jiang, Shuangpeng Wang, Binghui Li, Zhenzhong Zhang, Dongxu Zhao, Chong-Xin Shan, Bin Yao, and D. Z. Shen. p-type conductivity in n-doped zno: the role of the n(zn)-v(o) complex. *Physical Review Letters*, 108(21):215501, may 2012.
- [79] D. C. Look, G. C. Farlow, P. Reunchan, S. Limpijumnong, S. B. Zhang, and K. Nordlund. Evidence for native-defect donors in n-type zno. *Physical Review Letters*, 95(22):4, nov 2005.
- [80] D. C. Look, J. W. Hemsky, and J. R. Sizelove. Residual native shallow donor in zno. *Physical Review Letters*, 82(12):2552–2555, mar 1999.
- [81] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell. Characterization of homoepitaxial p-type zno grown by molecular beam epitaxy. *Applied Physics Letters*, 81(10):1830–1832, sep 2002.
- [82] David C Look. Electrical and optical properties of p-type zno. 20(4):S55.
- [83] David C Look, RL Jones, JR Sizelove, Nelson Y Garces, Nancy C Giles, and Larry E Halliburton. The path to zno devices: donor and acceptor dynamics. *physica status solidi (a)*, 195(1):171–177, jan 2003.
- [84] David C Look, Donald C Reynolds, JR Sizelove, RL Jones, Cole W Litton, G Cantwell, and WC Harsch. Electrical properties of bulk zno. *Solid State Communications*, 105(6):399–401, feb 1998.
- [85] Jinpeng Lv and Chundong Li. Evidences of vo, vzn, and oi defects as the green luminescence origins in zno. *Applied Physics Letters*, 103(23):–, dec 2013.
- [86] J. L. Lyons, A. Janotti, and C. G. Van de Walle. Why nitrogen cannot lead to p-type conductivity in zno. *Applied Physics Letters*, 95(25):252105, dec 2009.
- [87] J. L. Lyons, A. Janotti, and C. G. Van de Walle. Effects of hole localization on limiting p-type conductivity in oxide and nitride semiconductors. *Journal of Applied Physics*, 115(1):–, jan 2014.
- [88] M. D. McCluskey and S. J. Jokela. Defects in zno. *Journal of Applied Physics*, 106(7):13, oct 2009.
- [89] Matthew D. McCluskey, Caleb D. Corolewski, Jinpeng Lv, Marianne C. Tarun, Samuel T. Teklemichael, Eric D. Walter, M. Grant Norton, Kale W. Harrison, and Su Ha. Acceptors in zno. *Journal of Applied Physics*, 117(11):112802, mar 2015.
- [90] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Strassburg, M. Dworzak, U. Haboeck, and A. V. Rodina. Bound exciton and donor-acceptor pair recombinations in zno. *physica status solidi (b)*, 241(2):231–260, feb 2004.
- [91] B. K. Meyer, J. Stehr, A. Hofstaetter, N. Volbers, A. Zeuner, and J. Sann. On the role of group i elements in zno. *Applied Physics A*, 88(1):119–123, apr 2007.
- [92] S Misrachi, AR Peaker, and B Hamilton. A high sensitivity bridge for the measurement of deep states in semiconductors. *Journal of Physics E: Scientific Instruments*, 13(10):1055, oct 1980.

BIBLIOGRAPHY

- [93] S. K. Mohanta, A. Nakamura, and J. Temmyo. Nitrogen and copper doping in mgxzn1-xo films and their impact on p-type conductivity. *Journal of Applied Physics*, 110(1):8, jul 2011.
- [94] S. K. Mohanta, A. Nakamura, and J. Temmyo. Synthesis and characterization of n, in co-doped mgzno films using remote-plasma-enhanced metalorganic chemical vapor deposition. *Journal of Crystal Growth*, 375:1–5, jul 2013.
- [95] W. Mtangi, F. D. Auret, W. E. Meyer, M. J. Legodi, P. J. J. van Rensburg, S. M. M. Coelho, M. Diale, and J. M. Nel. Effects of hydrogen, oxygen, and argon annealing on the electrical properties of zno and zno devices studied by current-voltage, deep level transient spectroscopy, and laplace dlts. *Journal of Applied Physics*, 111(9):6, may 2012.
- [96] Wilfred Mtangi, FD Auret, M Diale, WE Meyer, A Chawanda, H De Meyer, PJ Janse Van Rensburg, and JM Nel. Effects of high temperature annealing on single crystal zno and zno devices. *Journal of Applied Physics*, 111(8):084503, apr 2012.
- [97] P. Muret, D. Tainoff, C. Morhain, and J. M. Chauveau. Donor and acceptor levels in zno homoepitaxial thin films grown by molecular beam epitaxy and doped with plasma-activated nitrogen. *Applied Physics Letters*, 101(12):4, sep 2012.
- [98] A. Nakagawa, F. Masuoka, S. Chiba, H. Endo, K. Megro, Y. Kashiwaba, T. Ojima, K. Aota, and I. Niikura. Photoluminescence properties of nitrogen-doped zno films deposited on zno single crystal substrates by the plasma-assisted reactive evaporation method. *Applied Surface Science*, 254(1):164–166, oct 2007.
- [99] A. Nakamura, T. Hayashi, A. Hierro, G. Tabares, J. M. Ulloa, E. Munoz, and J. Temmyo. Schottky barrier contacts formed on polar and nonpolar mgxzn1-xo films grown by remote plasma enhanced mocvd. *physica status solidi (b)*, 247(6):1472–1475, mar 2010.
- [100] A. Nakamura and J. Temmyo. Schottky contact on zno nano-columnar film with h(2)o(2) treatment. *Journal of Applied Physics*, 109(9):093517, may 2011.
- [101] H. Nakashima, D. Wang, T. Noguchi, K. Itani, J. L. Wang, and L. W. Zhao. Method for detecting defects in silicon-on-insulator using capacitance transient spectroscopy. *Japanese Journal of Applied Physics*, 43(5A):2402–2408, may 2004.
- [102] N. H. Nickel and M. A. Gluba. Defects in compound semiconductors caused by molecular nitrogen. *Physical Review Letters*, 103(14):4, sep 2009.
- [103] Alan V Oppenheim and Ronald W. Schafer. *Discrete-time signal processing*. Prentice-Hall, 1999.
- [104] S. Ozder, I. Atilgan, and B. Katircioglu. Effects of surface potential fluctuations on dlts of mos structure. *Solid-State Electronics*, 39(2):243–249, feb 1996.
- [105] S. Ozder, I. Atilgan, and B. Katircioglu. New approach to bias scan dlts for rapid evaluation of interface states in mos structures. *Solid-State Electronics*, 39(10):1507–1514, oct 1996.

- [106] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc. A comprehensive review of zno materials and devices. *Journal of Applied Physics*, 98(4):103, aug 2005.
- [107] Umit Ozgur, Daniel Hofstetter, and Hadis Morkoc. Zno devices and applications: A review of current status and future prospects. *Proceedings of the IEEE*, 98(7):1255–1268, jul 2010.
- [108] C. H. Park, S. B. Zhang, and S. H. Wei. Origin of p-type doping difficulty in zno: The impurity perspective. *Physical Review B*, 66(7), aug 2002.
- [109] John P Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, oct 1996.
- [110] John P Perdew, John A Chevary, Sy H Vosko, Koblar A Jackson, Mark R Pederson, Dig J Singh, and Carlos Fiolhais. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Physical Review B*, 46(11):6671, sep 1992.
- [111] Robert F Pierret and Gerold W Neudeck. *Advanced semiconductor fundamentals*, volume 6. Addison-Wesley Reading, MA, 2002.
- [112] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, A. I. Belogorokhov, E. A. Kozhukhova, A. V. Markov, A. Osinsky, J. W. Dong, and S. J. Pearton. Persistent photoconductivity in p-type zno(n) grown by molecular beam epitaxy. *Applied Physics Letters*, 90(13):132103, mar 2007.
- [113] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, E. A. Kozhukhova, H. S. Kim, D. P. Norton, S. J. Pearton, and A. I. Belogorokhov. Persistent photoconductivity in mgzno alloys. *Semiconductors*, 43(5):577–580, may 2009.
- [114] V. Quemener, M. Alnes, L. Vines, P. Rauwel, O. Nilsen, H. Fjellvag, E. V. Monakhov, and B. G. Svensson. The work function of n-zno deduced from heterojunctions with si prepared by ald. 45(31):315101.
- [115] V. Quemener, L. Vines, E. V. Monakhov, and B. G. Svensson. Electronic properties of vacancy related defects in zno induced by mechanical polishing. *Applied Physics Letters*, 99(11):112112, sep 2011.
- [116] V. Quemener, L. Vines, E. V. Monakhov, and B. G. Svensson. Iron related donor-like defect in zinc oxide. *Applied Physics Letters*, 102(23):232102, jun 2013.
- [117] V Quemener, L Vines, EV Monakhov, and BG Svensson. Evolution of deep electronic states in zno during heat treatment in oxygen-and zinc-rich ambients. *Applied Physics Letters*, 100(11):112108, mar 2012.
- [118] F. Reuss, C. Kirchner, T. Gruber, R. Kling, S. Maschek, W. Limmer, A. Waag, and P. Ziemann. Optical investigations on the annealing behavior of gallium- and nitrogen-implanted zno. *Journal of Applied Physics*, 95(7):3385–3390, apr 2004.
- [119] J. G. Reynolds, Jr. Reynolds, C. L., A. Mohanta, J. F. Muth, J. E. Rowe, H. O. Everitt, and D. E. Aspnes. Shallow acceptor complexes in p-type zno. *Applied Physics Letters*, 102(15):152114, apr 2013.

BIBLIOGRAPHY

- [120] R. Schifano, E. V. Monakhov, L. Vines, B. G. Svensson, W. Mtangi, and F. D. Auret. Defects in virgin hydrothermally grown n-type zno studied by temperature dependent hall effect measurements. *Journal of Applied Physics*, 106(4):043706, aug 2009.
- [121] M. Schirra, R. Schneider, A. Reiser, G. M. Prinz, M. Feneberg, J. Biskupek, U. Kaiser, C. E. Krill, K. Thonke, and R. Sauer. Stacking fault related 3.31-ev luminescence at 130-mev acceptors in zinc oxide. *Physical Review B*, 77(12):10, mar 2008.
- [122] M. Schmidt, H. von Wenckstern, R. Pickenhain, and M. Grundmann. On the investigation of electronic defect states in zno thin films by space charge spectroscopy with optical excitation. *Solid-State Electronics*, 75:48–54, sep 2012.
- [123] M. Schulz and N. M. Johnson. Transient capacitance measurements of hole emission from interface states in mos structures. *Applied Physics Letters*, 31(9):622–625, nov 1977.
- [124] Adel S Sedra and Kenneth Carless Smith. *Circuitos microelectrónicos*. New York: Oxford University Press, 5 edition, 2006.
- [125] Satoshi Shigemori, Atsushi Nakamura, Junji Ishihara, Toru Aoki, and Jiro Temmyo. Zn1-xcdxo film growth using remote plasma-enhanced metalorganic chemical vapor deposition. *Japanese journal of applied physics*, 43(8B):L1088, jul 2004.
- [126] We Shockley and WT Read Jr. Statistics of the recombinations of holes and electrons. 87(5):835, mar 1991.
- [127] J. C. Simpson and J. F. Cordaro. Characterization of deep levels in zinc-oxide. *Journal of Applied Physics*, 63(5):1781–1783, mar 1988.
- [128] C. S. Singh, G. Agarwal, G. D. Rao, S. Chaudhary, and R. Singh. Effect of hydrogen peroxide treatment on the electrical characteristics of au/zno epitaxial schottky diode. *Materials Science in Semiconductor Processing*, 14(1):1–4, mar 2011.
- [129] J. E. Stehr, X. J. Wang, S. Filippov, S. J. Pearton, I. G. Ivanov, W. M. Chen, and I. A. Buyanova. Defects in n, o and n, zn implanted zno bulk crystals. *Journal of Applied Physics*, 113(10):9, mar 2013.
- [130] D. Stichtenoth, J. Durr, C. Ronning, L. Wischmeier, and T. Voss. Characterization of the donor-acceptor-pair transition in nitrogen-implanted zinc oxide. *Journal of Applied Physics*, 103(8):5, apr 2008.
- [131] J. W. Sun, Y. M. Lu, Y. C. Liu, D. Z. Shen, Z. Z. Zhang, B. Yao, B. H. Li, J. Y. Zhang, D. X. Zhao, and X. W. Fan. Nitrogen-related recombination mechanisms in p-type zno films grown by plasma-assisted molecular beam epitaxy. *Journal of Applied Physics*, 102(4):6, aug 2007.
- [132] S. M. Sze. *Semiconductor devices, Physics of*. Semiconductor devices, Physics of. Wiley, 3rd. edition edition.

-
- [133] G. Tabares, A. Hierro, J. M. Ulloa, A. Guzman, E. Munoz, A. Nakamura, T. Hayashi, and J. Temmyo. High responsivity and internal gain mechanisms in au-znmgo schottky photodiodes. *Applied Physics Letters*, 96(10):3, mar 2010.
- [134] G. Tabares, A. Hierro, B. Vinter, and J. M. Chauveau. Polarization-sensitive schottky photodiodes based on a-plane zno/znmgo multiple quantum-wells. *Applied Physics Letters*, 99(7):071108, aug 2011.
- [135] D. Taïnoff, M. Al-Khalifioui, C. Deparis, B. Vinter, M. Teisseire, C. Morhain, and J. M. Chauveau. Residual and nitrogen doping of homoepitaxial nonpolar m-plane zno films grown by molecular beam epitaxy. *Applied Physics Letters*, 98(13):131915, mar 2011.
- [136] M. C. Tarun, M. Z. Iqbal, and M. D. McCluskey. Nitrogen is a deep acceptor in zno. *AIP Advances*, 1(2):7, jun 2011.
- [137] C. Ton-That, L. L. C. Lem, M. R. Phillips, F. Reisdorffer, J. Mevellec, T. . P. Nguyen, C. Nenstiel, and A. Hoffmann. Shallow carrier traps in hydrothermal zno crystals. *New Journal of Physics*, 16(8):083040, aug 2014.
- [138] M. Trunk, V. Venkatachalapathy, A. Galeckas, and A. Y. Kuznetsov. Deep level related photoluminescence in znmgo. *Applied Physics Letters*, 97(21):3, nov 2010.
- [139] A Tsukazaki, S Akasaka, K Nakahara, Y Ohno, H Ohno, D Maryenko, A Ohtomo, and M Kawasaki. Observation of the fractional quantum hall effect in an oxide. *Nature materials*, 9(11):889–893, oct 2010.
- [140] L. Vines, E. V. Monakhov, and B. G. Svensson. Effect of high temperature treatments on defect centers and impurities in hydrothermally grown zno. *Physica B: Condensed Matter*, 404(22):ABB; Adv Lab Solut; John Wiley & Sons; Monash Univ; Nelson MandelaEOLEOLMetropolitan Univ; S African Inst Phys; Univ Pretoria, dec 2009.
- [141] L. Vines, J. Wong-Leung, C. Jagadish, E. V. Monakhov, and B. G. Svensson. Ion implantation induced defects in zno. *Physica B: Condensed Matter*, 407(10):1481–1484, may 2012.
- [142] L. Vines, J. Wong-Leung, C. Jagadish, V. Quemener, E. V. Monakhov, and B. G. Svensson. Acceptor-like deep level defects in ion-implanted zno. *Applied Physics Letters*, 100(21):212106, may 2012.
- [143] Lasse Vines and Andrej Kuznetsov. Bulk growth and impurities. 88:67–104, 2013.
- [144] L. S. Vlasenko and G. D. Watkins. Optical detection of electron paramagnetic resonance in room-temperature electron-irradiated zno. *Physical Review B*, 71(12):125210, mar 2005.
- [145] H. von Wenckstern, R. Pickenhain, H. Schmidt, M. Brandt, G. Biehne, M. Lorenz, M. Grundmann, and G. Brauer. Deep acceptor states in zno single crystals. *Applied Physics Letters*, 89(9):092122, aug 2006.
- [146] M. R. Wagner, G. Callsen, J. S. Reparaz, J. H. Schulze, R. Kirste, M. Cobet, I. A. Ostapenko, S. Rodt, C. Nenstiel, M. Kaiser, A. Hoffmann, A. V. Rodina, M. R.
-

BIBLIOGRAPHY

- Phillips, S. Lautenschlager, S. Eisermann, and B. K. Meyer. Bound excitons in zno: Structural defect complexes versus shallow impurity centers. *Physical Review B*, 84(3):18, jul 2011.
- [147] K. L. Wang and A. O. Evwaraye. Determination of interface and bulk-trap states of IGFET's using deep-level transient spectroscopy. *Journal of Applied Physics*, 47(10):4574–4577, oct 1976.
- [148] L. J. Wang and N. C. Giles. Determination of the ionization energy of nitrogen acceptors in zinc oxide using photoluminescence spectroscopy. *Applied Physics Letters*, 84(16):3049–3051, apr 2004.
- [149] P. Wang, N. F. Chen, Z. G. Yin, R. X. Dai, and Y. M. Bai. p-type zn_{1-x}mg_xo films with sb doping by radio-frequency magnetron sputtering. *Applied Physics Letters*, 89(20):3, nov 2006.
- [150] S. Weiss and R. Kassing. Deep level transient fourier spectroscopy (DLTFS)—a technique for the analysis of deep level properties. *Solid-State Electronics*, 31(12):1733–1742, dec 1988.
- [151] G. Xiong, K. B. Ucer, R. T. Williams, J. Lee, D. Bhattacharyya, J. Metson, and P. Evans. Donor-acceptor pair luminescence of nitrogen-implanted zno single crystal. *Journal of Applied Physics*, 97(4):4, feb 2005.
- [152] K. Yamasaki, M. Yoshida, and T. Sugano. Deep level transient spectroscopy of bulk traps and interface states in si mos diodes. *Japanese Journal of Applied Physics*, 18(1):113–122, jan 1979.
- [153] Y. F. Yan, S. B. Zhang, and S. T. Pantelides. Control of doping by impurity chemical potentials: Predictions for p-type zno. *Physical Review Letters*, 86(25):5723–5726, jun 2001.
- [154] A. Zeuner, H. Alves, D. M. Hofmann, B. K. Meyer, A. Hoffmann, U. Haboeck, M. Strassburg, and M. Dworzak. Optical properties of the nitrogen acceptor in epitaxial zno. *physica status solidi (b)*, 234(3):R7–R9, dec 2002.
- [155] S. B. Zhang, S. H. Wei, and A. Zunger. Intrinsic n-type versus p-type doping asymmetry and the defect physics of zno. *Physical Review B*, 63(7):7, jan 2001.
- [156] A. Zunger. Practical doping principles. *Applied Physics Letters*, 83(1):57–59, jul 2003.