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Investigation of deep levels in bulk GaN

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ABSTRACT

The first gallium nitride (GaN) crystal was grown by hydride vapor phase epitaxy in 1969 by Maruska and Tietjen and since then, there has been an intensive development of the field, especially after the ground breaking discoveries concerning growth and p-type doping of GaN done by the 2014 year Nobel Laureates in Physics, Isamu Akasaki, Hiroshi Amano and Shuji Nakamura. GaN and its alloys with In and Al belong to a semiconductor group which is referred as the III-nitrides. It has outstanding properties such as a direct wide bandgap (3.4 eV for GaN), high breakdown voltage and high electron mobility. With these properties, GaN is a promising material for a variety of applications in electronics and optoelectronics. The perhaps most important application is GaN-based light-emitting-diodes (LED) which can produce a high-brightness blue light. Since the bandgap of GaN can be controlled by alloying it with aluminium (Al) or indium (In) for a larger or smaller bandgap, respectively, GaN is very important for optoelectronic applications from infrared to the deep ultraviolet region. There are other semiconductors with bandgap similar to GaN such as SiC, and the first commercially blue light emitting LEDs were manufactured in SiC, however, SiC has an indirect bandgap with a low efficiency of emitting photons, and today, the SiC based LEDs have been completely replaced by the considerable more efficient GaN based LEDs.

One problem, which has hampered the development of GaN based devices, is the lack of native substrate of GaN. Due to that, most of the GaN based devices are fabricated on foreign substrates such as SiC or Al_2O_3 . Growing on a foreign substrate results in high threading dislocation (TD) densities ($\sim 10^9 \text{ cm}^{-2}$) and stress in the GaN layer due to lattice mismatch and difference of thermal expansion coefficient between GaN and the substrate. The high TD density and the stress influence the performance of the devices.

Another important aspect related to GaN which has attracted many studies is how defects affect the efficiency of GaN-based devices. Therefore, it is necessary to understand the properties and to identify them. When we know their properties, one can estimate how they will influence the behavior of devices, and thereby, optimize the perfor-

mance of the device for its application. Basically, a fundamental knowledge of defect properties, and how to introduce them in a controlled manner, or to avoid them, is important in order to optimize the performance of devices. Defects can be introduced both intentionally and unintentionally into semiconductors during the growth process, during processing of the device or from the working environment, for example, devices working in a radioactive ambient are more likely to have defects induced by irradiation.

This thesis is focused on electrical characterization of defects in bulk GaN grown by halide vapor phase epitaxy (HVPE) by using deep level transient spectroscopy. Other measurement techniques like current-voltage measurement (IV), capacitance-voltage measurement (CV) and Hall measurement were also been used. Defects related to the growth process and the polishing process are discussed in *Paper 1*. In *Paper 2* and *Paper 3*, we focus on intrinsic defects in GaN introduced intentionally by electron irradiation. This type of defects are important since they can be unintentionally introduced during growth of the material, in the fabrication process of devices or if it is exposed to a radioactive environment. By electron irradiation, we can in a controlled manner introduce intrinsic defects for studies and by varying the electron beam energy and doses we can judge the nature of them. After electron irradiation, we observed several electrically active defects. These defects were characterized by DLTS to get important parameters such as activation energy, trap concentration, trap profile and capture cross-section. Especially, from temperature-dependent capacitance transient studies, we have determined the mechanism of the electron capturing process for some of them.

PREFACE

This Licentiate Thesis is a result of three years' work during my Ph. D. studies in Semiconductor Materials group at Linköping University. The project was financed by Swedish Energy Agency and the Swedish Research Council (VR). The results are presented in three included papers preceded by the introduction.

Linköping,

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INCLUDED PAPER

1. *Investigation of deep levels in bulk GaN material grown by halide vapor phase epitaxy*
T.T. Duc, G. Pozina, E. Janzén, and C. Hemmingsson
J. Appl. Phys. **114**, 153702 (2013).
2. *Radiation-induced defects in GaN bulk grown by halide vapor phase epitaxy*
T.T. Duc, G. Pozina, N.T. Son, E. Janzén, T. Ohshima and C. Hemmingsson
Appl. Phys. Lett. **105**, 102103 (2014).
3. *Capture cross-section of electron irradiation induced defect in GaN bulk grown by halide vapor phase epitaxy.*
T.T. Duc, G. Pozina, N.T. Son, E. Janzén, T. Ohshima and C. Hemmingsson
In manuscript.

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1. INTRODUCTION

Already in 1969, Maruska and Tietjen [1] started the development of GaN by successfully growing GaN on a sapphire substrate by Hydride (Halide) Vapor Phase Epitaxy (HVPE) method. However, due to problems in manufacturing of the material and doping, the development was hampered during the first 20 years. First in the beginning of the 90's, the technique to make GaN p-type was developed and after that, GaN has been extensively studied.

GaN is a semiconductor consisting of an III group element (Ga) and a V group element (N). GaN has a direct and large bandgap of 3.4 eV which depends on the temperature according to Varshni equation:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (1.1)$$

where $\alpha = 0.909$ meV/K and $\beta = 830$ K [2].

Moreover, the existence of AlN (a bandgap of 6.2 eV) and InN (a bandgap of 0.64 eV) enables the ability to easily control the width of the bandgap by making compound with aluminium (Al) for larger one and indium (In) for smaller one. This property makes it advantageous for optoelectronics devices working in short wavelength range [3]–[6] such as blue and ultraviolet (UV) light emitting diodes [5], laser diode [4], green light emitting devices [7] and UV photodetector [8]–[11]. In addition, GaN is also applied in the renewable energy field, particularly, making solar cells [12]–[14]. Other interesting properties are high breakdown field, high electron mobility and a high thermal conductivity. These properties opened up to new exciting applications for high-frequency and high-power devices such as transistors [8], [15]–[18], high electron mobility transistors (HEMT) [17][19] and ultrahigh power switches [8], [20]. Table 1.1 presents some basic parameters of several common semiconductors.

GaN is able to be grown by different methods depending on certain purpose, like metalorganic chemical vapor deposition (MOCVD) [21], molecular beam epitaxy (MBE) [22], hydride vapor phase epitaxy (HVPE) [23]–[25], high pressure solution growth (HPS) [26], [27], so-

dium (Na) flux [28], [29], and ammonothermal method [30]. These techniques (HPS, Na flux, ammonothermal method) is used for growing thick bulk GaN while MOCVD, MBE are often used in fabricating thin layers of GaN. The technique which has the largest growth rate is HVPE, see Table 1.2. Due to high growth rate, HVPE is the primary choice for growth of thick bulk GaN that can be used as high quality native substrate.

Table 1.1. Basic parameters for some common semiconductors are summarized from different sources [18], [31]–[38].

Semiconductor	Si	GaAs	SiC	GaN	AlN	InN	Diamond
Bandgap (eV)	1.1	1.4	3.25	3.4	6.2	0.64	5.46-5.6
Electron Mobility at 300K (cm ² /Vs)	1500	8500	700	1000-2000	300	3200	≤2200
Saturated Electron Velocity (× 10 ⁷ cm/s)	1	1.3	2	2.5			
Breakdown Field (MV/cm)	0.3	0.4	3	3.3	1.2-1.8	2	1-10
Dielectric constant	11.8	12.8	10	8.9-9.0	8.7	15.3	5.5
Thermal Conductivity (W/cmK)	1.5	0.5	4.5	>1.5	<2.85	0.45	6-20

Table 1.2. Features of some common growth techniques for growing bulk GaN

Growth Method	High pressure solution (HPS)[27][26]	Ammonothermal growth	Na-flux [28], [29],[39]	HVPE
Conditions	≤2GPa ≤ 1700°C	400 MPa 600°C	5-9.5 MPa 600-900°C	1 atm 1000-1100°C
Growth rate	0.1 μm/h in c-axis 0.1 mm/h - ⊥ c-axis	0.1 mm/day in<0001> [30]		100-500 μm/h in <0001>
Quality	High	High	High	Normal
Thickness	0.1 mm	cm-scale	< 10 mm	mm-scale
Mass pro-duction	Bad	Good	Good	Good
Cost	Expensive	Expensive	Expensive	Cheap

Since there is a lack of native substrates of GaN, foreign substrates such as sapphire or SiC are used. Due to the difference in lattice parameters of the substrate and GaN, the dislocation density in the material is high (in the order of $>10^9 \text{ cm}^{-2}$ for a $1\mu\text{m}$ thick layer). However, the dislocation density is dropping with thickness, and for a layer of 1 mm, the dislocation density is $\sim 10^6 \text{ cm}^{-2}$ which is necessary for fabrication of GaN based lasers. Another problem related to growth of GaN on a foreign substrate is the difference in thermal expansion that can cause fracture in the GaN during the cooling process. Due to the high growth rate of HVPE and good control of impurities, HVPE has shown to be the technique of choice in producing GaN substrates commercially.

The main problems in development of GaN-based applications today are the lack of native GaN substrate and how to make p-type GaN. There is possible to grow GaN, both from a solution or from gas phase. AMMONO company is growing and providing commercial GaN by the ammonothermal method which is a solution based technique. It gives GaN of high crystalline quality, nevertheless, the low growth rate and the use of high temperature and high pressure give rise to a high cost of the GaN substrates. Additionally, the high temperatures and the use of corrosive agents give rise to high impurity concentrations in the material. However, the dislocation density of such materials is very low ($\sim 10^4 \text{ cm}^{-2}$) which makes it interesting to be used as substrate material and recently, the AMMONO company demonstrated that ammonothermal grown GaN substrates can be used as seeds for HVPE growth[40]. Using this approach, crystalline material of high quality and low threading dislocation ($5 \times 10^4 \text{ cm}^{-2}$) was produced. Moving on to the question of p-doped GaN, the first p-type GaN with a hole concentration of $\sim 2 \times 10^{16} \text{ cm}^{-3}$ was fabricated in 1989 by Amano et al. [40] in which magnesium (Mg) was used as the dopant. They discovered that Mg was forming a complex with H during cooling after growth and in order to activate the Mg as p-dopant the GaN has to be annealed in a hydrogen-free atmosphere or irradiated by electrons. Other candidates for p-type dopant are Zn and Cd, however, the activation energy is too large to be acceptable for p-type doping due to high binding energy[41], [42](Zn $\sim 0.34 \text{ eV}$, Cd $\sim 0.55 \text{ eV}$). Therefore, Mg with its rather high thermal activation energy (0.17 eV)[43] is the only choice for acceptor even though just few percent of Mg is activated at room temperature.

Another important issue is the performance efficiency of GaN-based devices which is strongly affected by defects in the crystal. In the ideal case, we would like to grow perfect crystals with no defects. In fact, it is impossible to do. Defects always exist and they will influence the performance of GaN-based devices. To solve this problem, understanding the origin and the properties of them is necessary. From that knowledge, we can control the defect concentration in order to optimize and improve the devices performance. The defects are often dependent on growth technique, e.g., ammonothermal grown GaN has low concentration of structural defects when compared to others but high concentration of impurities, see [44]. There are a lot of studies on defects in GaN grown by other techniques such as MOCVD[45]–[47], MBE[48], [49] and HVPE [50]–[52].

Defects are not only coming from the growth process but they may also appear from the working environment. Many devices are widely used in radioactive environment such as in nuclear plants and in space. In this kind of environment, defects may be introduced and consequently, change the performance of the devices. Additionally, during processing of devices, ion-implantation and plasma etching techniques are used. In these types of techniques, high-energy particles are bombarding the surface which may give rise to defects in the material. To study and understand this kind of defects, irradiation technique is often used to intentionally create intrinsic defects in the material. In irradiation technique, an electron or ion beam (He, H ion)[53]–[67] are employed to irradiate the sample. The two main parameters that can influence on the creation of defects are the beam energy and the dose. The higher the energy, the more degree of damage appears in the sample. However, in ion beam techniques, also the direction of the beam may influence the depth profile of damage in the crystal. This effect is often referred as the "channelling" effect.

To study defects, deep level transient spectroscopy (DLTS) which was first proposed by Lang[68] has been shown to be a powerful method. Using DLTS, one can obtain important parameters of defects such as: activation energy, capture cross-section, depth profile and defect concentration. In **paper 1**, the properties of defects in HVPE-grown GaN were studied in details by deep level transient spectroscopy (DLTS) and other electrical characterization techniques[69]. In **paper 2**,

we have study electron-irradiation-induced defects in HVPE grown GaN and we report two new deep levels with high activation energy (D5I: 0.89 eV and D6: 1.14 eV) [70]. In **paper 3**, the capture cross-section of eletron-irradiation-induced defects was studied by the filling pulse width method.

2. PROPERTIES OF GaN

2.1. Crystal structure

GaN is a binary compound semiconductor which has two common polytypes: the zinc-blende (ZB) and wurtzite (WZ), see Fig. 2(a) and (b), respectively. In ZB phase, GaN has a space group of $F\bar{4}3m$ and each cubic unit cell consists of four Ga atoms and four N atoms. The unit cell contains two tetrahedrons in which N atom is surrounded by four Ga atoms and vice versa. The lattice constant of zinc-blende structure GaN thin films grown on (001) Si is about 4.49Å[71]. However, the ZB phase is not stable as the WZ phase that has a hexagonal unit cell. The ZB phase is only obtained when growing epitaxy thin films on (001) substrate. This leads to a high threading dislocation density and worsens the quality of film. In the thesis, we have studied bulk GaN with the stable WZ phase.

Figure 2.1. (a) zinc-blende structure and (b) wurtzite structure of GaN where Ga is illustrated as large green atom and N as small gray atom.

The space group for WZ is $P6_3mc$ in which the basic is comprised of two Ga atoms at $(0,0,0)$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$ and two N atoms at $(0, 0, \frac{3}{8})$ and $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2} + \frac{3}{8})$. The WZ structure is considered as the interpenetration of two hexagonal closed packed lattices of Ga and N (Fig. 2.2) where the distance between Ga and N along the direction $[0001]$ is $\frac{3}{8}c$ in ideal case. Here, c is the height of a hexagonal unit cell. The lattice constants at 300K are $a = 3.189 \text{ Å}$ and $c = 5.185 \text{ Å}$ and these constants depends

on the temperature and the doping concentration. Depending on which kind of structure, GaN has different properties, shown in Table 2.1. GaN has also one more polytype with rocksalt structure. However, the structure is not stable and the only condition to get this structure is under very high pressure and therefore, it has never been studied in detail.

Figure 2.2. Wurtzite structure of GaN shown as two interpenetrating lattice of Ga and N

Table 2.1. Basic properties of WZ GaN and ZB GaN[2][37]

Parameters	Wurtzite GaN	Zinc-blende GaN
Lattice constant [$\text{\AA}$]	$a = 3.189, c = 5.185$	4.5
The stacking order	AaBb along [0001] direction	AaBbCc along [111] direction
$P_{SP} (C/m^2)$	-0.034	
Effective density of states in the conduction band N_C (cm^{-3})	$N_C = 4.3 \times 10^{14} \times T^{\frac{3}{2}}$	$N_C = 2.3 \times 10^{14} \times T^{\frac{3}{2}}$
Effective density of states in the valence band N_V (cm^{-3})	$N_V = 8.9 \times 10^{15} \times T^{\frac{3}{2}}$	$N_V = 8.0 \times 10^{15} \times T^{\frac{3}{2}}$
Effective electron mass m_e	$0.20m_0$	$0.13m_0$
Effective mass of density of state m_v	$1.5m_0$	$1.4m_0$
Breakdown field at RT (Vcm^{-1})	5×10^6	$3.3 \div 5 \times 10^6$
Dielectric constant	8.9 (static) 5.35 (high frequency)	9.7 (static) 5.3 (high frequency)
Optical phonon energy (meV)	91.2	87.3

2.2. Polarity

2.2.1. The spontaneous polarization field

One property of GaN that is a major obstacle for light emitting devices, but very important for fabrication of AlGaIn/GaN HEMT structure is the spontaneous polarization field. The origin of the field is the no-inversion symmetry along the c-axis ([0001] direction). The lack of inversion symmetry is shown in Fig. 2.3 where it can be seen that the crystal can be terminated either with Ga- atoms or N-atoms depending on orientation. We refer the two faces as the Ga- face and the N-face, respectively. However, one thing that needs to be noticed is that it does not mean that the surface of the Ga-face or N-face does only consist of Ga or N-atoms, respectively. The polarity is determined by the direction of bonding from N atom to Ga atom along the c-axis. When a bond forms between Ga and N atoms by sharing electrons, these electrons have a tendency to be closer to the N atom. Thus, the volume close to the N atom is more negatively charged whereas the volume around the Ga atom is more positively charged. This gives rise to a dipole along the Ga-N bond. This electrical field is called spontaneous polarization because it exists without the presence of strain.

Figure 2.3. The hexagonal structure of Ga-polarity and N-polarity

2.2.1. Piezoelectric Polarity

One issue when a film is grown on a foreign substrate is the lattice mismatch which leads to stress in the film. The stress deforms the structure of the film and causes a piezoelectric field that contributes to the polarization. Therefore, the total polarization field consists of two components: one from spontaneous polarization ($\overrightarrow{P_{SP}}$) and one from piezoelectric polarization ($\overrightarrow{P_{PZ}}$)

$$\overrightarrow{P_{TOT}} = \overrightarrow{P_{SP}} + \overrightarrow{P_{PZ}} \quad (2.1)$$

The direction of the piezoelectric polarization depends on the relation of lattice between the film and the surface. If the film has a lattice constant smaller than the substrate, the film will be tensile strained and conversely, if the lattice constant is larger, the film will be compressively strained. The tensile strain results in a piezoelectric field vector which is parallel with the spontaneous polarization field vector while if the layer suffers from compressive strain, the vectors are antiparallel.

2.3. Basic properties

The most interesting property of GaN that makes it promising for optoelectronics applications, especially, blue and UV LEDs is the large direct bandgap of 3.4 eV. In LEDs, the light comes from the recombination of electrons locating around the minimum of the conduction band and holes locating around the maximum of the valence band, see Fig. 2.4. For a direct bandgap, the recombination process requires two particles: electron in the conduction band and hole in the valence band. For the indirect band, this process requires three particles: electron, hole and a phonon and that makes the probability for an electron-hole recombination significant lower and affects the efficiency of the light emitting process (Fig. 2.4). This is the reason why SiC, which has an indirect bandgap, is less suitable as a light emitter despite that the bandgap is similar to GaN. Another advantage of GaN is the possibility to control the bandgap by introducing Al or In which make it possible to fabricate LEDs with different wavelengths.

Other advantageous properties of GaN is a relatively high thermal conductivity, a high electron mobility and a high-breakdown field. The

value of thermal conductivity that has been reported in some studies and it varies in the range of 50-250 K/mW at room temperature [72]–[78] which is lower than the theoretically calculated value from Witek (et al.) [79]. However, this should be compared to SiC which has a thermal conductivity of 360 K/mW at room temperature [31]. The high mobility and high break down field open great opportunities of fabricating high-power and high-frequency devices like photodetector, transistors and switches [8], [10], [11], [15]–[20].

Figure 2.4. The diagram of (a) direct bandgap and (b) indirect bandgap in k-space

GaN is known as a compound having a high chemical stability, however, the chemical stability poses technological challenges for device processing. There have been many studies on etching of GaN with different etchants such as acids, bases, alkali solutions [80]–[85] at different temperatures and most of them showed an exceptional chemical stability of GaN. In early studies by Chu et al. [83], GaN was found to be dissolve in sodium hydroxide (NaOH). The main problem with this etchant is the formation of gallium hydroxide (GaOH) which is insoluble. Later, Pankove et al. tried to address this problem by electrolytic etching technique [80]. The quality of GaN significantly affects the ability of wet etching, particularly, the low quality has the high etching rate[86]. Another interesting behavior related to wet etching is the dependence of GaN polarity. In Palacios et al.’s report [87], using kali hydroxide (KOH) at 80°C, etching was only observed on the N-face and

not the Ga-face. Nowadays, phosphoric acid (H_3PO_4)[88], [89] is the most commonly used etchant in GaN device fabrication. The H_3PO_4 etching process is often carried out at the high temperatures ($\sim 190^\circ\text{C}$) with a etching rate varying in the range of 0.013 - 3.2 $\mu\text{m}/\text{min}$ [88].

3. GROWTH OF GaN

Since there is a lack of foreign substrates of GaN, almost all growth is done heteroepitaxially on foreign substrate materials such as sapphire, SiC or Si. This gives rise to several problems. One of issues is the difference in lattice parameters between GaN and the substrate which give rise to a high density of threading dislocations (TD). Additionally, the difference in thermal expansion coefficients between the substrate and the film causes stress in the layer after cooling to room temperature. This stress may give rise to deformation and cracks in the film. In order to overcome these problems, various types of buffer layers are commonly used in many growth techniques.

3.1. Metalorganic chemical vapor deposition (MOCVD)

Nowadays, MOCVD is known as the most common method to grow device structures in the semiconductor industry. This technique is preferred in growing thin layers due to several outstanding abilities. For example, by using MOCVD one can easily control a thickness by changing some basic parameters such as temperature, pressure, flow rate of precursor, etc.. Moreover, there exist a variety of pure precursors which makes it possible to grow some different types of semiconductors or other types of material. In principle, the MOCVD growth process consists of several basic steps which are mentioned below, see Fig. 3.1.

Figure 3.1. Precursor transport and reaction processes in conventional CVD

Precursors are transported directly to the reactor's region where precursor reacts with each other. Carrier gas is used for transporting the precursors.

1. Precursors react in gas phase and create gaseous by-products and reactants
2. Reactants are transported to the substrate surface by a diffusion process.
3. On the substrate surface, the transported reactants are adsorbed
4. Surface diffusion of reactants to growth sites.
5. Growth takes place on the surface by reactions.
6. The by-products from the reactions in step 5 are desorbed then evacuated away from the reaction zone.

In 1971, Manasevit et al.[90] reported his experimental results in which he used MOCVD for growth of GaN. In his study, Manasevit et al. used two different substrates (α -Al₂O₃ and α -SiC) heated to 925°-975° C. Trimethylgallium (TMG) and ammonia (NH₃) were employed as sources of Ga and N. However, the quality of GaN film at that time was not good due to an un-optimized growth process and low purity of the precursors.

The quality of GaN depends strongly on the quality of precursors and the substrates. Due to low cost, sapphire has been widely used as substrate even though the lattice mismatch is quite high. To deal with this problem, Amano and Akasaki [91] found a new method in which AlN was used as a buffer layer. This method has been widely and commercially used in growth of GaN until now. The buffer layer of GaN or AlN plays a role as a nucleation layer that absorbs the strain appearing during the growth process. The buffer layer has a thickness of few tens of nm and is often fabricated at low temperature in case of GaN.

In case of doping, MOCVD enables the possibility to easily dope the material by adding a organic compounds as a dopant source. In doping of GaN, Mg is used to make the material p-type and Si is used for n-type doping. In MOCVD system, bis-cyclopentadienylmagnesium (Cp₂Mg) and silane (SiH₄) are commonly used as a source of Mg and Si, respectively. These two compounds are transported to the substrate

by a carrier gas of H_2 , N_2 or a mixture of H_2/N_2 . Fig. 3.2 shows a diagram of MOCVD system using for doping Si or Mg.

Figure 3.2. Schematic diagram of the MOCVD process which SiH_4 and Cp_2Mg are used for growth of n-type and p-type GaN

3.2. Halide (Hydride) vapor phase epitaxy (HVPE)

HVPE has been used for growth of GaN for 45 years. The first successful growth of single crystal GaN was done by Maruska in 1969[1]. The characteristic of this technique is a high growth rate (100-500 $\mu m/hour$ along $\langle 0001 \rangle$ direction)[92] [92] which makes it as the preferred choice for growing thick GaN bulk material.

Many studies showed that high-quality GaN can be obtained by using HVPE in combination with other techniques. By using MOCVD grown GaN as starting layer, the initial growth is facilitated or by using ammonothermal growth substrate, the crystal quality is very high from the beginning of growth. . The quality of GaN crystal can be also improved by growing a low-temperature GaN buffer layer which is expected to reduce the propagation of threading dislocations from the GaN and the substrate interface[23].

All samples used for study in Paper 1-3 are thick free-standing GaN grown in a vertical hot wall HVPE reactor described in Fig. 3.3. The

chamber is made of quartz and divided into two zones (source zone and growth zone). In Linköping University's vertical HVPE reactor, the source zone which is heated by a resistive heater is at the lower part of the reactor. In the source zone, gallium chloride is formed by flowing HCl through a boat containing liquid Ga. The temperature of the source zone is often kept $\sim 800\text{-}900^\circ\text{C}$ at which the chemical reactions between Ga and HCl occurs as following:

The source zone's temperature decides which reaction should be predominant. By thermodynamic calculation, the reaction (3.1) is predominant when the temperature is above 500°C [93]. By keeping the temperature around $800\text{-}900^\circ\text{C}$, the efficiency of reaction (1) is very high[94]. This means that almost all HCl introduced into the Ga boat reacts with Ga.

When gaseous gallium chloride is formed, gallium chloride is transported to the growth zone through the quartz tube by a carrier gas of H_2 or H_2/N_2 . In the growth zone, a mixture of ammonia and H_2 is transported into the reaction region where ammonia reacts with gallium chloride to form GaN according to the below reaction:

One issue needs to address is the parasitic growth because the outlets of ammonia and gallium chloride are quite close. Consequently, ammonia easily reacts with gallium chloride to form GaN which deposits in the precursors inlet. If the GaN grown too thick, it will prevent precursors to enter the reactor. To address this problem, a flow of light gas (H_2 or H_2/N_2) is introduced between the ammonia tube and the gallium chloride, depicted in Fig. 3.3. This flow will prevent the ammonia gas from mixing with the gallium chloride before they arrive to the substrate.

Figure 3.3. Schematic diagram of a vertical HVPE reactor for growth of GaN [93] (move down)

4. DEEP LEVEL TRANSIENT SPECTROSCOPY

4.1. Metal-semiconductor junction (M-S junction)

In semiconductor devices, the M-S junction plays a very important role as the bridge between the semiconductor component and an external voltage source. Depending on the properties of the semiconductor and the metal, we can form a rectifying Schottky junction that only conducts current in one direction or a linear Ohmic junction where the current is linearly dependent on the applied voltage. In order to fabricate a Schottky diode, we need both a Schottky and an Ohmic junction, see Fig. 4.1. In the thesis, all samples used for electrical characterization are prepared as Schottky diodes to which consist of two kinds of MS junction. Since we are only using n-type GaN, we will restrict the discussion to n-type Schottky diodes. Therefore, this part will focus on the characteristics of the n-type Schottky diode which is fabricated by making a contact between metal and n-type GaN semiconductor, as shown in Fig. 4.1. The applied voltage V_a can be negative or positive depending on working condition.

Figure 4.1. Structure of GaN Schottky diode

To understand the principle of forming barrier between semiconductor and metal, it is convenient to use an energy band diagram. Fig. 4.2(a) shows the flat band diagrams of metal and an n-type semiconductor. There are some important notations needed to be described here. E_{Fm} and E_{Fs} are the Fermi level of the metal and semiconductor, respectively. ϕ_m, ϕ_s are the work function of the metal and the semiconductor, respectively. The work function is the potential between the Fermi level and the vacuum level (E_{vac}). χ is the electron affinity (EA) defining the energy needed to remove a electron in the conductor band edge (E_C) to

the vacuum level. Depending on the work function ϕ_m of the metal and the electron affinity χ of the semiconductor, the M-S junction can behave as a Schottky or an Ohmic junction. For GaN, the EA is determined by theoretical calculation to about 1.44 eV [95] and 1.88 eV [96]. However, these values are much lower than the experimental value which is about 4.1 eV at room temperature [37]. Fig. 4.2.(b) shows the flat band diagram after forming a contact between metal and n-type semiconductor. Observe that the thermal equilibrium condition is not considered in this figure. Here is ϕ_B the barrier height which is the difference between the metal work function and the affinity of the semiconductor:

$$\phi_B = \phi_m - \chi \quad (4.1)$$

The barrier height is the potential between the Fermi level of the metal and the conduction band edge. Therefore, the value of the barrier height is dependent on the metal. The barrier height of some metals which is commonly used for making Schottky diode on n-type GaN is shown in Table 4.1.

To form a Schottky contact on n-type GaN, there are two requirements that need to be fulfilled:

- The doping concentration is not too high
- The work function of the metal has to be greater than the one of the n-type semiconductor.

Table 4.1. Summary some important parameters of metal commonly used for making contact with n-type GaN[97]–[99]

Metal	Au	Ni	Pt	Ti	Al	In	Ag
Work function	5.1	5.15	5.65	4.33	4.08	4.09	4.26
Barrier height	0.87-0.98	0.95-1.13	1.01-1.16	-	-	-	-
Contact	Shottky	Shottky	Shottky	Ohmic	Ohmic	Ohmic	Ohmic

Figure 4.2. Flat band diagrams of the metal and semiconductor in the case of no contact (a) and making a contact (b).

In Fig. 4.3(a), the thermal equilibrium condition is taken into account and we obtain a thermal equilibrium diagram in which a bending of the band is observed. When a metal having a higher work function touches a semiconductor, higher energy electrons in the semiconductor will diffuse through the junction to the metal and create a diffusion current. This leaves positive ionized donors in the semiconductor which results in forming an electric field. This field will create a drift current. The diffusion of electrons continues until the electric field is high enough to prevent electrons in the semiconductor from further diffusion. Thus, the diffusion current is equal to the drift current and the Fermi levels in the metal and the semiconductor are equal in thermal equilibrium. At this time, a barrier for the carrier is formed to hinder further electron diffusion between the two regions, as depicted in Fig. 4.3(a).

The term V_i in Fig. 4.3 is called the built-in potential which is the energy needed to be supplied to an electron in the semiconductor to surmount the potential barrier. The built-in potential for a metal-semiconductor junction in this case is obtained by the equation below [100]:

$$V_i = \phi_M - \chi - \frac{E_C - E_{fs}}{q} = \phi_B - \frac{kT}{q} \ln \frac{N_C}{N_d} \quad (4.2)$$

where k is the Boltzmann constant, q the charge of the carrier, T the temperature, N_d the donor concentration and N_C is the effective density of states in the conduction band which is calculated by [101]:

$$N_C = 2 \left[\frac{2\pi m_e^* kT}{h^2} \right]^{3/2} \quad (4.3)$$

where h is Plank constant and m_e is the effective electron mass. For n-GaN Schottky, it is convenient to use the approximate equation [102]:

$$V_i = \frac{1}{3} \left(3.503 + \frac{5.08 \times 10^{-4} T^2}{T - 996} \right) \text{ (eV)} \quad (4.4)$$

Figure 4.3. The thermal equilibrium diagram (a) and the positive ionized donor region (b) for a n-type Schottky diode

4.2. Depletion region

In the thermal equilibrium state, there is a region formed in the semiconductor in which there is no free carrier. This region is called the depletion region. In principle, the depletion region extends to the metal region, however, the extension into the metal is negligible due to the much greater electron concentration than the doping concentration in the semiconductor [103]. The depletion width W can be calculated by using Poisson's equation and for the case of a Schottky contact it is given by:

$$W = \sqrt{\frac{2\varepsilon_r\varepsilon_0V_i}{qN_d}} = \sqrt{\frac{2\varepsilon V_i}{qN_d}} \quad (4.5)$$

where ε , ε_r , ε_0 are the permittivity, the relative permittivity (also called electric constant, $\varepsilon_r(\text{GaN}) = 8.9$), the vacuum permittivity ($\varepsilon_0 = 8.86 \times 10^{-12} \text{ F/m}$), respectively; $q = 1.6 \times 10^{-19} \text{ C}$ is the elementary charge; N_d is the donor concentration and V_i is the built-in potential.

Figure 4.4. Band diagram of n-type Schottky contact under a forward bias (a) and a reverse bias (b)

Another important behavior of the depletion region is the dependence on the applied voltage. The depletion width widens when a reverse bias applies to Schottky diode and shortens in case of a forward bias. Fig. 4.4 illustrates the behavior of the bending band when applying a forward bias and a reverse bias. The depletion width in the cases of a forward bias and a reverse bias is calculated by the equation (4.6) and (4.7), respectively.

$$W_f = \sqrt{\frac{2\varepsilon_r\varepsilon_0(V_i - V_f)}{qN_d}} \quad (4.6)$$

$$W_r = \sqrt{\frac{2\epsilon_r\epsilon_0(V_i + V_r)}{qN_d}} \quad (4.7)$$

When working with characterization techniques like capacitance-voltage measurement (CV), deep level transient spectroscopy (DLTS) which will be mentioned in later, we indirectly measure the width W of the depletion region by measuring the capacitance.. From the capacitance, one can obtain some important parameters such as the depth profile of doping concentration or defect concentration. The equation for calculating the capacitance C of the depletion region is given below [103] in which the depletion region is considered as the capacitance of two parallel plates with area A :

$$C = \frac{\epsilon_r\epsilon_0 A}{W} \quad (4.8)$$

4.3. Defects in GaN

In all crystals, we have defects and GaN is no exception. Some of them are introduced intentionally since we want to change the property of the material (i.e. by doping), while others may be introduced unintentionally during growth, by the ambient or during processing of the material. Fig. 4.5 depicts some common defects in semiconductor crystal: (1) vacancy, (2) self-interstitial, (3) foreign interstitial, (4) foreign substitutional, (5) stacking fault, (6) dislocation, (7) precipitate, (8) interstitial type dislocation loop, (9) vacancy type dislocation loop. Defects (1)-(4) and (5)-(9) are called point defects and line defects, respectively.

Referring to point defects, it is necessary to distinguish two definitions: intrinsic defects and extrinsic defects. For intrinsic point defects, a host atom at a certain position is missing and leaves a vacancy behind or a host atom occupies an interstitial site to form self-interstitial defect. For extrinsic point defects, the origin of this defect relates to foreign atoms which can take a lattice or interstitial site. Foreign atoms which can be introduced unintentionally or intentionally into the semiconductor are called impurities or solutes, respectively.

Figure 4.5. Defects in semiconductor crystal (based on [107][115])

For GaN, these defects are commonly introduced in the growth process, during device processing and by the working environment. Defects affect strongly the performance of GaN-based devices, and therefore, it is essential to understand the properties and the origin of defects which opens up the ability to control the behavior of devices. The thesis will focus on intrinsic defects which may be introduced during growth, device processing or by the working environment.

By introducing defects in the crystal, energy levels which are localized in the proximity to the defect are formed. If the energy level is close to the edge of the conduction or valence band, defects are refereed as shallow. These defects are used to control the concentration of charge carriers and can be introduced by doping with a suitable element (e.g. Si for n-type GaN, Mg for p-type GaN). In the case of defects with energy levels locating deeply in the band gap (>100 meV), they are called deep level defects. Fig. 4.6 shows the presence of deep levels in the semiconductor band structure. Deep levels in the upper half of the band gap often have a higher probability of capturing electrons in the conduction band whereas deep levels in the lower half of the band gap have a higher probability of capturing holes in the valence band.

Figure 4.6. Band structure diagram of the undoped semiconductor and the doped semiconductor with a presence of deep levels caused by defects where E_i is the intrinsic Fermi level, E_F is the Fermi level of the n -type and p -type semiconductor, E_d and E_a are the level of donors and acceptors, ET is the electron trap, HT is the hole trap.

4.4. Emission and capture of charge carriers

The emission and capture process of charge carriers can be described by the Shockley-Read-Hall statistics [104], [105]. There are four processes which can happen as a deep level is introduced into the band gap: (a) the capture of electrons from the conduction band, (b) the emission of electrons from the trap center, (c) the emission of holes to the valence band or the emission of electrons from the valence band to the trap center, (d) the capture of holes from the valence band. Fig. 4.7 describes the emission and capture of electron and hole by a deep level in the band gap in which n and p are the concentrations of electrons and holes in the conduction band and valence band, respectively, p_T and n_T are the concentration of the empty trap and the filled traps, $c_n n$ and $c_p p$ are the capture rate of electron and hole, $e_{n,p}$ are the *emission rate* of electron and hole. These terms of c_n and c_p are called the capture coefficient which has the unit of cm^3/s and is defined by:

$$c_{n,p} = \sigma_{n,p} \langle v_{th} \rangle \quad (4.9)$$

where v_{th} is the thermal velocity of electron or hole, $\sigma_{n,p}$ is the capture cross-section of the deep level.

By combining the four capture and emission processes, we can form some important specific cases. A combination of process (a) and (b) or process (c) and (d) is the trap case. A generation event appears when the process (b) occurs followed by the process (d). The third case is the recombination in which the process (c) occurs after the process (a), or vice versa. If the recombination and the generation occur together, the impurity is viewed as a G-R center (Generation-Recombination center). It is important to distinguish the behavior of an impurity if it acts as a trap or a G-R center. For the trap case, just one band (conduction band or valence band) and the impurity participated while two bands and the impurity for the case of the G-R center.

Figure 4.7. Emission and capture processes of electron and hole at the trap level locating into the band gap of the semiconductor.

4.5. Time dependence of the occupancy of traps

Emission and capture lead to a change of the carrier concentration (n , p) and the concentration of filled trap centers (n_T). Therefore, it is important to determine the relation between n , p and n_T and consider the case of how the electron concentration in the conduction band changes. The number of electrons can increase by electron emission from the trap level or decreases by electron capture (case b and a, respectively, in Fig. 4.7). The net change of electrons in the conduction band is the differ-

ence between these two processes. Thus, the rate equation can be written as:

$$\frac{dn}{dt} = (b) - (a) = e_n n_T - c_n n p_T \quad (4.10)$$

In analogue with Eq. 4.10, the rate equation for holes has a similar form and is given by the net change of holes in the valence band:

$$\frac{dp}{dt} = (d) - (c) = e_p p_T - c_p p n_T \quad (4.11)$$

To determine how the concentration of filled traps is changing with time ($\frac{dn_T}{dt}$), we can use the relations how electron and hole concentration is changing with time, (Eq. (4.10) and Eq. (4.11), respectively). The concentration of filled traps decreases with an increase of the electron concentration which is related to the emission process of electron from the trap center. Opposite to that, when the trap center emits a hole to the valence band, it leaves a filled trap center behind. For this reason, the rate of change of the filled trap center is given by the difference between these two processes:

$$\begin{aligned} \frac{dn_T}{dt} &= \frac{dp}{dt} - \frac{dn}{dt} = e_p p_T - c_p p n_T - e_n n_T + c_n n p_T \\ &= (e_p + c_n n)(N_T - n_T) - (c_p p + e_n) n_T \end{aligned} \quad (4.12)$$

where $N_T = p_T + n_T$ is the total defect concentration.

4.6. Temperature dependent emission rate

Most of the papers in the thesis are focused on electron traps in n-type GaN, for this purpose, it is useful to formulate the electron emission rate from Eq. (4.12). Actually, it is not easy to solve Eq. (4.12) without doing simplifications. First, electron traps are considered in thermal equilibrium at which the principle of detailed balance is used. Therefore, there is no change in the number of electron traps in thermal equilibrium because the capture rate of electron (hole) must be equal to the emission rate of electron (hole). Thus, we have:

$$e_p(N_T - n_T) = c_p p n_T \quad (4.13)$$

$$e_n n_T = c_n n (N_T - n_T) \quad (4.14)$$

From that, the ratio of n_T/N_T can be expressed as the function of capture rate and emission rate as:

$$\frac{n_T}{N_T} = \frac{e_p}{e_p + c_p p} = \frac{c_n n}{e_n + c_n n} \quad (4.15)$$

Using Fermi-Dirac distribution function[103], the degree of occupancy of traps is given:

$$\frac{n_T}{N_T} = \left[1 + \frac{g_0}{g_1} \exp\left(\frac{E_T - E_F}{kT}\right) \right]^{-1} \quad (4.16)$$

Where g_0, g_1 are the degeneracy factors of the deep level when being empty or occupied by an electron, respectively. From Eq. 4.15 and 4.16, the electron emission rate is derived:

$$e_n = c_n n \frac{g_0}{g_1} \exp\left(\frac{E_T - E_F}{kT}\right) \quad (4.17)$$

The electron concentration in the conduction band is expressed by [106]:

$$n = N_C \exp\left(-\frac{E_C - E_F}{kT}\right) \quad (4.18)$$

where N_C is the effective density of states in the conduction band and valence band:

$$N_C = 2M_C \left(\frac{2\pi m_e^* k_B T}{h^2} \right)^{1/2} \quad (4.19)$$

where M_C is the number of conduction band minima of the semiconductor (for wurzite GaN $M_C = 1$), m_e^* is the effective mass of electron. Substituting c_n in Eq. 4.17 by $\sigma_n v_{th}$ in Eq. 4.9, the electron emission rate can be rewritten as:

$$e_n = \sigma_n \langle v_{th} \rangle \frac{g_0}{g_1} N_C \exp\left(-\frac{E_C - E_T}{kT}\right) \quad (4.20)$$

where $\langle v_{th} \rangle$ is the rms thermal velocity of electron and hole:

$$\langle v_{n,p} \rangle = \left(\frac{3k_B T}{m_e^*} \right)^{1/2} \quad (4.21)$$

Combination of Eq. 4.19, 4.20, 4.21, it is convenient to rewrite the emission rate as following:

$$e_n = \frac{g_0}{g_1} \sigma_n \gamma T^2 \exp\left(-\frac{E_C - E_T}{kT}\right) \quad (4.22)$$

where $\gamma = 2\sqrt{3} \left(\frac{2\pi}{h^2} \right)^{\frac{3}{2}} m_n^* k^2 M_C$. Eq. 4.22 is “the heart” of DLTS from which the activation energy and the capture cross-section can be determined.

4.7. Capacitance transient spectroscopy

The basic principle of capacitance transient spectroscopy is based on monitoring a time-dependent change of the charge density in the space charge region of a diode. The width of the space-charge region W is dependent on the charge density and, therefore, the change can be recorded as a change of the diode capacitance since the width is related to the capacitance according to Eq. 4.8. The thermal emission of trapped charge carriers in the space-charge region make the capacitance of a p-n or Schottky diode change and it results in a capacitance transient that is recorded and analyzed to obtain important information of the trap such as activation energy, capture cross-section and trap concentration.

The principle is shown in details in Fig. 4.8. Firstly, (1) a fixed reverse bias V_r is applied to the diode in order to remove electrons from traps in the depletion region. Next, (2) a voltage pulse, named a filling pulse V_f , is introduced to fill all traps below the Fermi level. After the pulse ends, (3) the reverse bias is restored. The free electrons are rapidly swept out from the depletion region while the removals of trapped electrons are governed by the thermal emission from the trap level. During

the emission process, the capacitance of the depletion region changes as the function of time according to [107]:

$$C(t) = C_r \left[1 - \frac{n_{T0}}{2N_D} \exp\left(-\frac{t}{\tau_e}\right) \right] \quad (4.23)$$

Where n_{T0} is the density of filled traps at $t=0$, C_r the capacitance of the diode when all traps are empty at V_r , τ_e is the emission time constant, and $\tau_e = \frac{1}{e_n}$. Eq. 4.23 describes the capacitance transient, and is used to determine important defect parameters.

Figure 4.8. Band diagram of a Schottky diode for (a) reverse bias, (b) zero bias, (c) reverse bias at $t = 0$, the applied voltage on a Schottky diode (d) and the capacitance behaviour of a Schottky diode (e)

4.8. Deep level transient spectroscopy

Deep level transient spectroscopy which was introduced by Lang[68] in 1974 is the most powerful and widely used capacitance transient technique in characterization of electrically active traps in semiconductors. In DLTS, which is a correlation technique, we are multiplying the capacitance transient with reference signal known as the weighting function ($F_{corr}(t)$) and the resulting signal is integrated.

$$S = \frac{1}{T} \int_0^T C(t) F_{corr}(t) dt \quad (4.24)$$

where T is the period of the weighting function. By doing this the signal-to-noise can be improved and we can determine traps with low concentrations. The simplest case of weighting function has the form:

$$F_{corr}(t) = \delta(t - t_1) - \delta(t - t_2) \quad (4.25)$$

where $\delta(t - t_i)$ is the Kronecker delta and t_1 and t_2 two different time points. Solving Eq. 4.24 with the weighting function of Eq. 4.25 and noticing that $T = t_2 - t_1$, the DLTS output signal is:

$$S = C(t_2) - C(t_1) \quad (4.26)$$

The two different time points define something that is called the rate window. The emission rate from the trap is temperature dependent, and therefore, the time constant of the capacitance transient. When the emission rate corresponds to the rate window, the DLTS signal $S(T)$ will show a peak related to that trap as shown in Fig. 4.9. Actually, the rate window contains information about the emission rate which is chosen as a reference value.

When substituting $C(t)$ in Eq. 4.26 by Eq. 4.23, the DLTS output is:

$$S(t) = C_r \frac{n_{T0}}{2N_D} \left[\exp\left(-\frac{t_2}{\tau_e}\right) - \exp\left(-\frac{t_1}{\tau_e}\right) \right] \quad (4.27)$$

To get the condition for the maximum peak, differentiation of $S(t)$ with respect to τ_e is used:

$$\frac{dS(t)}{d\tau_e} = C_r \frac{n_{T0}}{2N_D \tau_e^2} \left[t_2 \exp\left(-\frac{t_2}{\tau_e}\right) - t_1 \exp\left(-\frac{t_1}{\tau_e}\right) \right] = 0 \quad (4.28)$$

Solving Eq. 4.28, the relationship between $\tau_{e(max)}$ and the rate window is obtained:

$$\tau_{e(max)} = \frac{t_1 - t_2}{\ln\left(\frac{t_1}{t_2}\right)} \quad (4.29)$$

Therefore, by choosing the rate window, it is possible to determine the emission rate through the time constant. Each emission rate corresponds to a certain temperature at which the DLTS peak occurs. By varying the sampling time t_1 and t_2 so that the reference constant time changes, a series of DLTS spectra are obtained in which the DLTS peak move to the left (lower temperature) or the right (higher temperature), corresponding to an increase or decrease of the reference constant time, respectively. This is useful for identify the activation energy of the trap as we will show later.

Figure 4.9. The DLTS spectrum obtained from analysis of the capacitance transients

4.9. Output parameters of DLTS measurements

4.9.1. Activation energy

When characterizing defects, one important parameter is the activation energy, which is the energy needed to empty the trap. The way of determining the activation energy is based on Eq. 4.22. After taking the natural logarithm of the expression can be written as:

$$\ln\left(\frac{e_n}{T^2}\right) = \ln\left(\frac{g_0}{g_1} \sigma_n \gamma\right) - \frac{E_C - E_T}{kT} = \ln\left(\frac{g_0}{g_1} \sigma_n \gamma\right) - \frac{E_A}{kT} \quad (4.30)$$

From Eq. 4.30, it is possible to extract the activation energy by using a semi-logarithmic plot of $\ln\left(\frac{e_n}{T^2}\right)$ versus $\left(\frac{1000}{T}\right)$, named an Arrhenius plot. To construct the Arrhenius plot, a series of DLTS spectra are obtained by changing the window rate. An example is shown in Fig. 4.10(a). Next, the temperature of each peak minima/maxima and the corresponding emission rate is plotted in an Arrhenius plot, shown in Fig. 4.10(b). By linear fitting using Eq. 4.30, we can determine the activation energy E_A and a rough estimate of the capture cross-section σ_n .

Figure 4.10. A series of the DLTS spectra corresponding to different window rates (a) and the Arrhenius plot derived from the DLTS spectra.

4.9.2. Capture cross-section

The relationship between the emission rate and the capture cross-section in Eq. 4.30 is commonly used to determine capture cross-section. By finding the intercept of the Arrhenius plot and the vertical axis, the capture cross-section is obtained. However, the capture cross-section derived from Eq. 4.30 is not very accurate because it does not take into account of the dependence of the emission rate on the Gibbs energy. Thus, the intercept point actually gives a value of $\sigma_{n, effective} = \sigma_n \exp\left(\frac{\Delta S}{k}\right)$ which means that the value from Eq. 4.30 is only a rough estimate of the capture cross-section. To get the accurate capture cross-section, the value from Eq. 4.30 has to be divided by the term of $\exp\left(\frac{\Delta S}{k}\right)$. In many cases, the capture cross-section is dependent on temperature which makes the situation even more complex. In many capturing processes the capture cross-section can be described by the relationship below [108]:

$$\sigma_n = \sigma_{T \rightarrow \infty} \exp\left(-\frac{E_{a\sigma}}{kT}\right) \quad (4.31)$$

where $\sigma_{T \rightarrow \infty}$ is the capture cross-section when the temperature goes to infinity and $E_{a\sigma}$ is the capture cross-section barrier. Consequently, Eq. 4.22 can be rewritten in the form which the dependence of the emission rate on the Gibbs free energy and the temperature, more details of description is presented in Ref. [107]:

$$e_n = \frac{g_0}{g_1} \sigma_{T \rightarrow \infty} \exp\left(\frac{\Delta S}{k}\right) T^2 \exp\left(-\frac{\Delta H + E_{a\sigma}}{kT}\right) \quad (4.32)$$

where ΔS and ΔH are the entropy and the enthalpy, respectively.

Even if the method using the intercept point for evaluation does not give the exact value, however, it has been widely used in many reports for estimating a rough value of σ_n .

In order to get a more accurate estimate of σ_n , a technique suggested by Criado et. al. [109] can be used. In this technique, the DLTS peak

amplitude is measured as the function of different filling pulse width. By using very short filling pulses, all traps will not have time to capture carrier and we will therefore only get a DLTS signal from filled traps. By plotting the DLTS amplitude as a function of the filling pulse width, we can determine the capture cross-section. Depending on which kinds of defect (point defect or extended defect), the relationship between the DLTS signal and the filling pulse width is written as below:

For point defect[69],[110], [111]:

$$S_{peak}(t_f) = S_1[1 - \exp(-\sigma_n n \langle v_{th} \rangle t_f)] + S_2 \ln(S_3 t_f) \quad (4.33)$$

where $S_{peak}(t_f)$ is the DLTS peak corresponding to the filling pulse width t_f , S_1 , S_2 and S_3 are the parameters in which S_1 is related to the trap concentration, S_2 and S_3 are related to the free carrier tail. These three parameters are determined by fitting the function of S_{peak} versus t_f by using Eq. (4.32).

For extended defect[69][110], [112]:

$$S_{peak}(t_f) = S_4 \ln(t_f) \quad (4.34)$$

where S_4 is determined by fitting

4.9.3. Trap concentration

Another important parameter is the trap concentration. This information is quite straight forward to obtain from the DLTS spectrum since the peak amplitude of the defect is proportional to the trap concentration. However, the DLTS technique is just suitable for the trap concentration much less than the donor concentration. The trap concentration can be calculated by [107]:

$$N_T = \frac{|S_{peak}|}{C_r} \frac{2r^{\frac{r}{r-1}}}{1-r} N_d \quad (4.35)$$

Where S_{peak} is the amplitude of the DLTS peak and $r = t_2/t_1$. The expression is evaluated from Eq. 4.27 and Eq. 4.29. Observe that Eq.

4.35 is only valid if the filling pulse is long enough to fill all defects in the investigated part of the depletion region.

However, the trap concentration can be affected by the free carrier tail which is located at the edge of the depletion region, where the free carrier concentration is gradually decreasing. This can be considered as a free carrier tail into the depletion region. This region extends a distance of λ from the edge of the depletion region to the point at which the Fermi level crosses the trap level ($E_F = E_T$), see in Fig. 4.8(a). The width of this region in steady state is given by [113]:

$$\lambda = \sqrt{\frac{2\varepsilon_r\varepsilon_0}{q^2N_d}(E_F - E_T)} \quad (4.36)$$

It is obvious that the transition region is independent with the applied voltage which means this region, for a certain trap level and a uniform donor concentration, is constant whether the diode is under a reverse or forward bias. In the case of low electric field (a reverse bias is small) where the depletion width is a little larger than the transition region, it will affect the accuracy of DLTS measurement, particularly, the trap concentration calculated from a DLTS spectrum is not correct. In that case, it is necessary to add a λ -related correction. However, the transition region can be neglected when the depletion width in the case of a high electric field is much larger than the transition region.

In the case of taking into account of the influence of the free charge carrier tail, the equation for calculating the trap concentration needs to be modified. If we assume that the depletion widths caused by a reverse bias and a filling voltage are W_r and W_f , respectively, only the traps in the region of $(W_r - \lambda)$ and $(W_f - \lambda)$ are monitored by the DLTS method. Thus, the real trap concentration now is given by:

$$N_{T,real} = \frac{W_r^2}{(W_r - \lambda)^2 - (W_f - \lambda)^2} N_T \quad (4.37)$$

All the trap concentrations in **Paper 1** is corrected by Eq. 4.37.

5. OTHER TECHNIQUES

5.1. Current – voltage measurement (IV)

The DLTS technique requires a good quality of Schottky diode which has a low leakage current. This is due to the strong influence of the leakage current on the capacitance measurement which can lead to serious errors in analysis of the DLTS spectrum[114]. Some problems related to leakage current are reduction of the peak amplitude, a shift of the peak position and broadening of peaks which may give rise to wrong trap concentration, activation energy. To assess the property of the Schottky diode, IV is widely used. All samples in the thesis were characterized by IV measurement to make sure that the leakage current is under a value of $10\text{ }\mu\text{A}$ [103].

Figure 5.1. Current-voltage measurement of two different Schottky diodes in the range of -10V to 10V, the insert shows the scaled up range of -10V to 0V.

Fig. 5.1 shows the IV data of two Schottky diodes which demonstrates rectifying properties. However, only one of the diodes fulfills the requirement for carrying out DLTS measurements (diode 1). Diode 2 is not good for DLTS measurements since the leakage current at -10V is too high ($> 250\text{ }\mu\text{A}$). This can seriously affect the accuracy of the parameters obtained from DLTS.

5.2. Capacitance – voltage measurement (CV)

As mentioned in section 4.7.3, the donor concentration is needed for calculation of the trap concentration. To get the donor concentration, it is quite convenient and simple to use a CV measurement. The principle of this measurement relies on the relationship between the depletion region capacitance and the donor concentration which is shown below [103]:

$$\frac{1}{C^2} = \frac{2V}{A^2 \epsilon_r \epsilon_o q N_d} = \frac{2(V_r + V_i)}{A^2 \epsilon_r \epsilon_o q N_d} \quad (5.1)$$

where A is the area of the contact, C is the capacitance, N_d is the net donor concentration, ϵ_r, ϵ_o are the relative permittivity (also called electric constant, $\epsilon_r(GaN) = 8.9$), the vacuum permittivity ($\epsilon_o = 8.86 \times 10^{-12} F/m$), respectively, V is total voltage, V_r is the reverse bias, V_i is the built-in potential and q is the elementary charge. From Eq. 5.1, it is apparent that the slope of the $1/C^2$ versus V plot can provide the donor concentration. The built-in potential is also obtained from this plot by extrapolating the line to the crossing point of the voltage axis.

6. SUMMARY OF PAPERS

Paper 1: Deep levels in free-standing GaN grown by halide vapor phase epitaxy were electrically characterized by using deep level transient spectroscopy (DLTS). Six electron traps with activation energy derived from the Arrhenius plot were observed in the DLTS spectrum: E_1 ($E_C - 0.252$ eV), E_2 ($E_C - 0.53$ eV), E_3 ($E_C - 0.69$ eV), E_4 ($E_C - 0.65$ eV), E_5 ($E_C - 1.4$ eV), and E_6 ($E_C - 1.55$ eV). Among them, trap E_4 and trap E_6 which has not been previously reported is suggested to be introduced by the polishing process. The capture cross-section of trap E_1 , E_2 , E_4 was determined by using the filling pulse width technique. From the behavior of the DLTS signal vs the filling pulse width plot, it is suggested that these traps probably are associated with point defects. These capture cross-sections were temperature independent.

Paper 2: Electron-irradiation-induced defects in bulk GaN grown by halide vapor phase epitaxy were investigated by deep level transient spectroscopy. The sample was irradiated by 2MeV electron at a fluence of 1×10^{14} cm². The traps, labeled D2 ($E_C - 0.24$ eV), D3 ($E_C - 0.60$ eV), D4 ($E_C - 0.69$ eV), D5 ($E_C - 0.96$ eV), D7 ($E_C - 1.19$ eV), and D8, were observed before performing irradiation. Three electron-irradiation-induced traps, labeled as D1 ($E_C - 0.12$ eV), D5I ($E_C - 0.89$ eV), and D6 ($E_C - 1.14$ eV), were observed. Among the three irradiation-induced traps, the trap D1 has previously been reported few times and suggested to be associated with the nitrogen vacancy. The D5I and D6 centers are suggested to be related to primary intrinsic defects due to their the annealing behavior.

Paper 3: A thick GaN grown by halide vapor phase epitaxy was irradiated by 2 MeV at a fluence of 5×10^{14} cm² and then characterized by deep level transient spectroscopy. The paper focused on determining the capture cross-section and its temperature dependence of electron-irradiation-induced deep levels by the filling pulse method. After irradiation, four deep trap levels, labelled ET1 ($E_C - 0.178$ eV), ET2 ($E_C - 0.181$ eV), ET3 ($E_C - 0.256$ eV) and ET5 were observed. After annealing at 650K for 2 hours, only two deep levels ET1 and ET4 were detected. The temperature behavior of the deep level ET1 showed that the capturing process is probably related to the multiphonon process whereas the capture cross-section of the deep levels of ET2 and ET3 is not dependent on the temperature.

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