# Characterization and Manipulation of N-face Gallium Nitride Etching in Alkaline Solution

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## Zusammenfassung

Galliumnitrid (GaN) ist das Schlüsselmaterial zur Herstellung blauer und weißer Leuchtdioden (LEDs). Ein wichtiger Schritt bei ihrer Herstellung ist die Erzeugung einer rauen GaN-Oberfläche. Dadurch wird die Effizienz der Lichtemission signifikant erhöht. Tatsächlich wird die interne Totalreflexion der erzeugten Photonen an der flachen Grenzfläche zwischen GaN und Luft durch Aufrauen der Oberfläche minimiert. Ein üblicher Ansatz zur Entwicklung der Letzteren ist das nasschemische Ätzen in wässriger KOH Lösung bei erhöhter Temperatur. Dieser Prozess wurde in der Literatur in den letzten 30 Jahren eingehend diskutiert und wurde dennoch noch nicht vollständig verstanden. Ein präziseres Verständnis der GaN Ätzreaktion in KOH würde eine kontrolliertere Prozessumgebung und damit eine effizientere Steigerung der Lichtauskopplung aus den LEDs ermöglichen.

Diese Arbeit konzentriert sich auf die Charakterisierung der GaN Ätzreaktion in wässriger KOH Lösung. Dabei liegt das Hauptaugenmerk auf der polaren N-face Kristallfacette, die nach epitaktischem GaN Wachstum durch Laser Lift Off (LLO) freigelegt wird. Nasschemisches Aufrauen ist immer noch eine sehr attraktive Alternative zum oft angewendeten trockenchemischen Ätzen. Durch die Nutzung des intrinsischen Bestrebens von N-Face GaN, während des Ätzens eine raue Oberfläche durch Bildung hexagonaler Pyramiden zu entwickeln, kann eine höhere Kosteneffizienz im Vergleich zur zeit- und materialintensiven Kombination von Photolithographie und Plasmaätzen erzielt werden.

Nach einer Einführung in die Eigenschaften der Nitride der 3. Hauptgruppe des Periodensystems sowie in den industriellen Standard der LED Produktion wird der Wissensstand vor Beginn der aktuellen Studie zusammengefasst und eingehend diskutiert.

In Kapitel 4 werden die verwendeten experimentellen Materialien und Methoden detailliert vorgestellt. Als grundlegendes Werkzeug für die hochpräzise Analyse der zeitaufgelösten GaN Ätzrate wird eine neuartige Methode unter Verwendung der induktiv gekoppelten plasmaoptischen Emissionsspektroskopie (ICP-OES) entwickelt. Die Methode basiert auf der Messung gelösten Galliums in der KOH Lösung und überwindet die Hauptnachteile der bisherigen literaturbekannten Methoden zur Bestimmung der GaN Ätzrate. Im Vergleich zu literaturbekannten Methoden ist der wichtigste Nutzen der neuen Methode, dass der Ätzprozess für eine Probennahme zur ICP-OES Analyse nicht unterbrochen werden muss. In Ätzpausen kann es somit nicht zur Anoxidation der Oberfläche und einer resultierenden Verfälschung des nachfolgenden Prozessschrittes kommen. Außerdem wird unabhängig von der Oberflächenrauigkeit der durchschnittliche GaN Abtrag bestimmt. Ein negativer Einfluss der Rauigkeit, wie er bei profilometrischen Abtragsmessungen zustande kommt, wird somit wirksam umgangen.

In Kapitel 5 wird die Ätzkinetik verschiedener epitaktischer GaN Schichtstapel zeitaufgelöst analysiert, was durch die neue ICP-OES Methode erstmals ermöglicht wird. Auf diese Weise werden sowohl die Einflüsse der epitaktischen Wachstumsbedingungen als auch von Ansätzen zur Verringerung der Kristalldefektdichte auf die Ätzrate einzelner epitaktischer Schichten aufgeklärt. Darauf aufbauend wird die Wechselwirkung zwischen Versetzungsdefekten und den individuellen Positionen entstehender Ätzstrukturen untersucht.

In Kapitel 6 werden zwei verschiedene Ansätze zur Vorbehandlung von GaN Wafern vorgestellt, um durch den LLO verursachte Oberflächenschäden zu beseitigen. Das mechanische Polieren von GaN wird als wirksames Werkzeug zur Erhöhung der Ätzreproduzierbarkeit während der industriellen Prozessierung präsentiert.

Der Einfluss der Prozessparameter KOH Konzentration, Temperatur und Umwälzung der Lösung auf das Ätzverhalten des verwendeten Versuchsmaterials wird in Kapitel 7 untersucht.

Die molekulare Ätzreaktion wird in Kapitel 8 anhand der Analyse von Reaktanden und Reaktionsprodukten aufgeklärt. Auch die Ursache für das anisotrope Ätzen, das zur Pyramidenbildung führt, wird auf atomarer Ebene erklärt. Hierbei werden literaturbekannte Konzepte weiterentwickelt, um ein umfassendes Bild zu generieren.

Der elektronische Einfluss auf die lokale Ätzrate wird schließlich in Kapitel 9 verwendet, um die Ätzrate zu manipulieren. In einem neuartigen und bei Veröffentlichung der Arbeit bereits patentierten Prozess wird durch Elektronenbestrahlung der GaN Oberfläche vor dem Ätzen die lokale Ätzrate signifikant verringert. Es wird die erfolgreiche Strukturierung der GaN Oberfläche mit Punkt-, Linien-, Kreis- und individuellen Formen vorgestellt.

Zusammenfassend schafft diese Studie ein besseres und präziseres Verständnis des nasschemischen GaN Ätzprozesses bis auf atomare Ebene. Es werden grundlegende Einblicke in die Ätzreaktion generiert, um einen stabileren und reproduzierbareren Ätzprozess zu erzielen. Die Arbeit zielt durch erstmalig durchgeführte Experimente darauf ab, die Lichtproduktion in der modernen Welt durch Anwendung neuester wissenschaftlicher Untersuchungen noch effizienter als heute zu gestalten.

### Abstract

Gallium nitride (GaN) is the key material for the production of blue and white light emitting diodes (LEDs). An important step during their production is the creation of a rough GaN surface. Thereby, light emission efficiency is significantly increased. Effectively, total internal reflection of generated photons on the flat interface between GaN and air is minimized by surface roughening. A common approach for the development of a rough surface is wet-chemical etching in aqueous KOH solution at elevated temperature. This process has been discussed thoroughly in literature for the last 30 years and still has not yet been entirely understood. A precise understanding of the GaN etch reaction in KOH would enable a more controllable process and thereby a more efficient enhancement of the light extraction from the LEDs.

This work focuses on the characterization of the GaN etch reaction in KOH solution. Thereby, the polar GaN N-face is the key material, which is revealed after epitaxial GaN growth by laser lift-off (LLO). To this day, wet-chemical roughening represents a very attractive alternative for the often applied dry-chemical roughening. Utilizing the intrinsic endeavor of N-face GaN towards the development of surface roughness during etching by formation of hexagonal pyramids, much higher cost efficiency can be achieved compared to a time- and material-intensive combination of photolithography and plasma etching.

After an introduction into the properties of group-III nitrides as well as the industrial standard for LED processing, the state of knowledge prior to the current study is extensively reviewed.

In chapter 4, the employed experimental materials and methods are presented in detail. As a fundamental tool for the high-precision analysis of the time-resolved GaN etch rate (ER), a novel method is developed utilizing inductively coupled plasma-optical emission spectroscopy (ICP-OES). The method is based on the measurement of dissolved Ga in KOH solution and overcomes major disadvantages of previously reported methods for ER determination. Compared to literature-known methods, the most important advantage of the ICP-OES method is that sample taking can be carried out without having to interrupt the etch process. Thereby, no surface oxidation can occur in etch process disruptions, that would lead to a resulting distortion of the subsequent etch step due to a higher dissolution rate of the respective  $GaO_x$  species. Also, the average GaN removal is determined regardless of surface roughness. The negative influence of surface roughness on the precision or profilometric methods is thereby circumvented.

The etch kinetics of multiple epitaxial GaN layer stacks are analyzed in chapter 5 in a time-resolved manner. This experiment is enabled for the first time by the developed ICP-OES method. Thereby, the influence of both epitaxial growth conditions and approaches towards crystal defect density reduction on the ER of individual epitaxial layers are clarified. Based on that, the interaction between dislocation defects and the individual positions of surface structures is investigated.

In chapter 6, two different approaches for pretreatment of GaN wafers are presented for the removal of surface damage caused by LLO. Mechanical polishing is proposed to be an effective tool to increase the etch reproducibility during industrial processing.

The influence of process-parameters (i.e., KOH concentration, temperature and solution agitation) on the etch behavior of the applied GaN material system is examined in chapter 7.

An in-depth investigation of the molecular etch reaction is presented in chapter 8 based on the analysis of reactants and reaction products. Also, the root cause for anisotropic etching, which leads to pyramid formation, is explained on the atomic level. Hereby, literature known concepts are further elaborated to create an overall understanding.

The electronic influence on the local ER is finally used in chapter 9 to manipulate the local ER. This novel process will already be patented by the time this thesis is published. The local ER is significantly decreased by electron irradiation on the GaN surface prior to etching. Successful structuring of the GaN surface with point-, linecircular and individual shapes is presented.

In conclusion, this study creates a better and more precise understanding of the wetchemical GaN etch process down to the atomic level. Fundamental insight into the etch reaction is presented to achieve a more stable and reproducible etch process. By unprecedented scientific investigations, this work aims towards making light production in the modern world even more efficient than today.

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### **1** Introduction

Today's modern world is walking on a road of digitalization. Every year, a great variety of new electronics for consumer as well as professional applications is developed and put on the market. All of them are designed for productivity and efficiency. Some are intended to support the comfort and physical health of the individual man and woman. With the steadily increasing number of humans, we as a society face the responsible handling of the planet earth - our most important resource - as the biggest task of the present time.

Within the last 30 years, the development of the light emitting diode (LED) has played a very important role in the modernization of lighting. Constant effort of many scientists and companies has created a light source exceeding the efficiency of the conventional light bulb many times over. At the latest, the stepwise legal prohibition of light bulb sales, which was established by the European Union in the year 2009, emphasized the importance of LEDs for the present and future light generation.

Blue and white LEDs share gallium nitride (GaN) as the principle material system. GaN is a semiconductor with a band gap energy of  $3.4 \,\mathrm{eV}$  at room temperature (RT) and emits ultraviolet (UV) light with a wavelength of 365 nm under application of electric current. Both a lower band gap energy  $E_g$  of 450 nm and a higher internal quantum efficiency are introduced by a multi quantum well (MQW) utilizing the ternary semiconductor indium gallium nitride [1]. Visible blue light, which is emitted by the latter system, can subsequently be transformed into white light by deposition of a yellow fluorescent phosphorus compound on top of the GaN chip surface. Both emission spectra of the blue LED and the yellow phosphorus layer add up to white light.

The efficiency of a LED, however, is not only made up by its internal quantum efficiency. The latter only represents the selectivity of electrically introduced electron-hole pairs

#### 1 Introduction

to undergo radiative recombination. Two more terms play a very important role. The external quantum efficiency makes a statement about the ease of generated photons to escape the chip and participate in the light emission. Also, the efficiency of the chip package comprising different approaches for lens and mirror geometry allows for an ideally directed light emission to perfectly adapt the component to the particular application.

The morphology of the chip surface plays a major part in the external quantum efficiency. The refractive indices of air and gallium nitride exhibit values of n = 1.0 and  $n \approx 2.5$ , respectively. This leads to a small light escape cone of 23.6° relatively to the chip surface. Only photons which are generated within this certain light escape cone can leave the chip. In contrast, photons created outside of the escape cone suffer total internal reflection. The latter causes the majority of photons to be absorbed in the chip sidewalls. A drastic increase in outcoupling efficiency of up to 300 % was achieved by roughening the GaN surface. Roughening generates a larger surface area as well as multiple additional surface angles that photons can trespass. A common method for surface roughening of GaN is wet-chemical etching in alkaline solution, e.g., aqueous (aq.) KOH, TMAH, NaOH. The etchant shows selectivity between different crystal facets of GaN so that the hexagonal crystal symmetry is translated into a surface comprising hexagonal pyramids with side plane angles of 61° relatively to the flat plane. This etch process has been applied in industry for many years. However, still no deep understanding of the mechanism and the multiple material- and process-dependent influences on magnitude and reproducibility of the etch rate (ER) could be obtained. Lacking reproducibility always leads to expensive and time consuming combinations of stepwise roughening and weighing to achieve a certain specified etch depth. This clearly shows the necessity to further investigate this technology.

**Objectives** During the course of this work, the wet-chemical etch process of GaN is analyzed to evaluate the influence of material variation and process control on ER and resulting surface morphology. First, the epitaxial growth conditions of the substratenear GaN buffer layers are varied. Their influence on the etch kinetics in aq. KOH solution is measured. For the measurement of etch kinetics, a novel high-precision inductively coupled plasma-optical emission spectroscopy (ICP-OES) method is developed. The latter is based on the determination of dissolved Ga in KOH solution. Also, the influence of surface damage induced by laser lift-off (LLO) processing on the etch reproducibility is quantified for the first time. Based on these findings it is rated, which steps must be made to remove inconsistency from the ER and which parameters can be changed without having a negative impact on reproducibility. For the determination of the ER dependency on process-dependent influences (i.e., KOH concentration, solution temperature and solution agitation), a standard GaN sample material is presented to achieve an optimum etch reproducibility for the resolution of minor process changes. After characterization of the material- and process-influences on the ER, the etch reaction is investigated on the atomic level. Also, the underlying reason for ER variation between the different crystal facets is investigated and discussed. Finally, the electronic influence on the GaN etching behavior is considered. Electron irradiation on GaN prior to etching is applied to manipulate the local ER and effectively structure the surface, which opens up a field of unprecedented processing capabilities. This concept is proven to have great potential for future applications with structuring requirements on a nm scale.

### 2.1 Structural Properties

Group-III elements B, Al, Ga and In form binary nitrides with the composition  $A^{III}N$ , whereby  $A^{III} = B$ , Al, Ga or In [2]. In principle, three crystal structures are possible for these materials, i.e., wurtzite, zinc-blende and rock-salt type. Zinc-blende and rock-salt systems stem from  $\alpha$ -ZnS and NaCl, respectively, and represent cubic unit cells. At ambient conditions, however, the hexagonal wurtzite structure is the thermodynamically stable phase, whereby each element is coordinated tetragonally (Figure 2.1, left). It is also the most important modification during industrial processing.

The wurtzite unit cell is described by two lattice parameters a and c with a theoretical ratio resulting from hexagonal close packing of spheres.

$$\frac{c}{a} = \sqrt{\frac{8}{3}} = 1.633$$
 (2.1)

Actual group-III nitrides deviate from this ideal value due to lattice instability and



Figure 2.1: Wurtzite crystal structure of group-III nitrides (left). Black and blue balls represent A<sup>III</sup> and N atoms, respectively. Lattice parameters a and c of wurtzite AlN, GaN and InN (right) [3, 4].

ionicity [5]. Experimentally obtained lattice parameters are given for  $A^{III} = Al$ , Ga and In (Figure 2.1, right) [3].

Lattice distortion from the ideal wurtzite lattice also varies with stoichiometry of ternary nitrides, that are of equal industrial importance, e.g.,  $In_xGa_{1-x}N$  or  $Al_xGa_{1-x}N$  [6]. As the atom radius increases with atomic number from B to In, the unit cell becomes larger as well. The dependency of the lattice constants on the molar ratio of group III elements is thereby linear. The Vegard's law describes this linear dependency for both mentioned ternary alloys [5].

$$a (Al_x Ga_{1-x} N) = (3.189 - 0.086 x) \text{\AA}$$
 (2.2)

$$c (Al_x Ga_{1-x} N) = (5.188 - 0.208 x) \text{\AA}$$
 (2.3)

$$a (In_x Ga_{1-x}N) = (3.1986 + 0.3862 x) \text{\AA}$$
 (2.4)

$$c(\text{In}_{x}\text{Ga}_{1-x}\text{N}) = (5.226 + 0.574 x) \text{\AA}$$
 (2.5)

The wurtzite type crystal lattice formed by materials with more than one atom type lacks inversion symmetry. The most stable growth direction during epitaxial preparation is in c-direction, which is polar. The two polar c-crystal facets with Miller indices (0001) and  $(000\overline{1})$  hereby equal the III- and N-polar crystal facets of a bulk crystal [7–10]. Crystal polarity can be controlled by growth conditions [11]. Considering Figure 2.1, left, the top and bottom surfaces represent III- and V-polarity, respectively. This assumes that black and blue spheres are A<sup>III</sup> and N atoms. Polarity is not equivalent to termination of the surface, which describes the chemical composition of the surface. A III-polar crystal facet can still be terminated with nitrogen atoms. Each symmetrically equivalent set of crystal facets has individual chemical properties including stability against etching, which will play a major role in the experiments conducted during the course of this work.

			Plane letter	Miller indices	Polarity
[000]]		C	С	(0001)	polar
	<b>F</b>	n/r/n	m	$\{10\overline{1}0\}$	nonpolar
			S	$\{10\overline{1}1\}$	semipolar
	[1120]		r	$\{10\overline{1}2\}$	semipolar
			a	$\{1\overline{2}10\}$	nonpolar
			n	$\{1\overline{2}13\}$	semipolar

Figure 2.2: Common facets of wurtzite crystals and their respective plane nomenclature letters (left). Miller indices and polarity of common wurtzite crystal planes (right) [5, 12, 13].

Miller Indices for Crystal Vector and Facet Identification For the identification and explanation of vectors and crystal planes/facets, Miller indices are used during the course of this work. They are explained in detail in the following. 1D Vectors and 2D facets are distinguished by the type of bracket (Table 2.1).  $[a_1a_2a_3c]$  represents a single vector.  $(a_1a_2a_3c)$  represents a single crystal plane, respectively.  $\langle a_1a_2a_3c \rangle$  refers to a single vector  $[a_1a_2a_3c]$ , but includes all other vectors, which are symmetrically equivalent to the former. In the same way,  $\{a_1a_2a_3c\}$  summarizes all symmetrically equivalent crystal planes to  $(a_1a_2a_3c)$ . The wurtzite crystal lattice has a hexagonal symmetry. Thus, the specific crystal facet  $(10\overline{11})$  has five other equivalent facets, which can be received by rotation of the hexagonal unit cell. The equivalent facets can be easily determined by variation of the first three digits' order  $a_1$ ,  $a_2$  and  $a_3$ within the brackets. E.g., the term  $\{10\overline{11}\}$  summarizes the following six specific crystal planes  $(10\overline{11})$ ,  $(1\overline{1}0\overline{1})$ ,  $(0\overline{1}1\overline{1})$ ,  $(01\overline{11})$ ,  $(\overline{1}10\overline{1})$  and  $(\overline{1}01\overline{1})$ . In the same way, the example  $\langle 10\overline{1}0 \rangle$  summarizes the six specific vectors  $[10\overline{1}0]$ ,  $[1\overline{1}00]$ ,  $[01\overline{1}0]$ ,  $[0\overline{1}10]$ ,  $[\overline{1}100]$ and [1010]. The four digits  $a_1, a_2, a_3$  and c indicate the relative direction in three lateral dimensions  $a_1$ ,  $a_2$  and  $a_3$  as well as the z-direction c (Figure 2.3, left). The

Bracket type	Geometric element	Example
$\boxed{a_1a_2a_3c}$	Single vector	$[10\overline{1}0]$
$\langle a_1 a_2 a_3 c \rangle$	Set of symmetrically equivalent vectors	$\langle 10\overline{1}0\rangle$
$(a_1a_2a_3c)$	Single crystal plane	(0001)
$\{a_1a_2a_3c\}$	Set of symmetrically equivalent crystal planes	$\{10\overline{11}\}$

 Table 2.1: Bracket types of Miller indices for representation of single vectors, crystal planes and the sum of all symmetrically equivalent vectors and planes.

actual material-dependent dimensions of a and c are equivalent to the crystal lattice parameters a and c (Figure 2.1, right). The partial travel length into each dimension results in the nomenclature of a vector  $[a_1a_2a_3c]$ . E.g., [0001] refers to 0 steps into each a direction and 1 unit cell length into c direction (Figure 2.3, center). Crystal planes are characterized by their normal vector intersecting the respective facet with a 90° angle. The nomenclature of the lateral Ga-face (0001) is indicated by its normal vector [0001] (Figure 2.3, right). For the comprehension of a crystal facet based on its Miller indices, the consideration of its intersections with the axes  $a_1, a_2, a_3$  and c is very helpful. Thereby, not the absolute values of the intersections with  $a_1$ ,  $a_2$ ,  $a_3$  and c must be taken into account, but the reciprocal values. The (0001) plane, for example, does not cross the three lateral axes  $a_1$ ,  $a_2$  and  $a_3$ . Therefore, the hypothetical intersections have coordinates of  $\infty$  and reciprocal values of 0, the latter of which are found in the Miller indices. The c-axis is intersected at c=1, which is equivalent to a reciprocal value of 1. Considering the green  $(1\overline{1}01)$  facet in Figure 2.3, right, both axes  $a_1$  and c intersect the plane at their coordinates 1. The direction of the  $a_3$ -axis is parallel to the plane resulting in an intersection of  $\infty$  and a reciprocal value 0. In the third example, the blue  $(\overline{1}2\overline{1}0)$  facet, both  $a_1$  and  $a_3$  intersect the plane at -1 (Figure 2.3, right). The  $a_2$  axis is intersected at a coordinate of  $a_2 = 0.5$ , the reciprocal value of which is 2. Again, c does not intersect at all, which results in  $\infty$  and a reciprocal value of 0.



Figure 2.3: Schematic explanation and examples for the Miller nomenclature of crystal vectors and facets.

### 2.2 Electronic Properties

Depending on their electronic properties, materials are classified as metals, semiconductors and insulators. Hereby, semiconductors have a specific resistance between metals and insulators [14]. They are able to conduct electricity, but only if sufficient energy is applied to the material (e.g., by temperature or optical excitation) [7]. At 0 K, all electrons are located at the atom cores. At room temperature (RT), some valence electrons absorb enough heat to be separated from the atom cores and are able to move along the crystal lattice [15]. Thus, the counterpart of mobile electrons are equally mobile holes, which are located at the positively charged atom core. Hole mobility is based on a mechanism of reverse migrating electrons from adjacent atom cores to the more positively charged ones. The combination of both electron and hole species is called electron-hole pair. If voltage is applied to the semiconductor, both electrons and holes contribute to the resulting current flow.

#### 2.2.1 Band Model

The electronic characteristics in solid materials are explained by the band model. In a two-atom situation, the atomic orbitals of both atoms can overlap positively or negatively. Hereby, the positive overlap yields the bonding molecular orbital with a lower energy compared to the foregoing atomic orbitals. Negative overlap forms the anti-bonding molecular orbital, that is higher in energy. The number of molecular orbitals in a multi-atom complex is equivalent to the number of atoms. If not two but many atoms form a solid, positive and negative combination of atomic orbitals form energy bands instead of single molecular orbitals (Figure 2.4) [16]. The orbital band, which is low in energy and provides bonding of the atoms, is called valence band (VB). The high-energy orbital providing electrical conduction, is called conduction band (CB), respectively. The band energies are indicated by  $E_{VB}$  and  $E_{CB}$ .

The Fermi energy  $E_F$  marks the orbital, which has the highest energy at 0 K and is occupied by electrons at the same time. In conducting materials (e.g., metals) VB and VB overlap. Thus, the activation energy needed for an electron to reach a non-occupied orbital is very low. At RT, many electrons are excited and provide excellent electrical conduction along the metal.



Figure 2.4: Schematic band models of conductors (e.g., metals), semiconductors and insulators (e.g., diamond, ceramics). Orbitals occupied by electrons are marked in gray. The Fermi energy  $E_F$  represents the highest energetic orbital that is occupied at 0 K. The band gap energy  $E_g$  equals the difference between the highest valence band orbital and the lowest conduction band orbital. It is the activation energy  $E_a$  for electrical conduction of a semiconductor [14].

In semi-conducting materials, the band gap energy  $E_g$  has a value which can be overcome by energy intake, as it was mentioned above.  $E_g$  marks the difference between the highest valence band and the lowest conduction band orbitals. At RT, small quantities of electrons, that are present in the conduction band, supply moderate electrical conduction (small circles in Figure 2.4, center). Common semiconductors and their band gap energies  $E_g$  are shown in Table 2.2. GaN has a direct band gap with an energy of 3.4 eV, which equals a wavelength of 365 nm. This wavelength is in the UV range of the light spectrum. In case of radiative recombination of a hole in the VB and an excited electron in the CB, the energy is released in form of an emitted photon with an energy of  $E_g$ . In ternary semiconducting alloys,  $E_g$  follows the molar composition in a slightly non-linear dependency. For  $In_xGa_{1-x}N$  the following empirical correlation was found.

$$E_{g}(In_{x}Ga_{1-x}N) = x \cdot E_{g}(InN) + (1-x) \cdot E_{g}(GaN) - b(InGaN) \cdot x \cdot (1-x)$$
(2.6)

Hereby,  $E_g$  (In<sub>x</sub>Ga<sub>1-x</sub>N),  $E_g$  (GaN) and  $E_g$ (InN) represent the band gap energy values of the respective compounds. The bowing parameter b was empirically determined to be 1.43 eV assuming  $E_g$  (InN) = 0.7 eV. By careful tuning of the group-III element ratio, any light wavelength between  $E_g$  (AlN) and  $E_g$  (InN) can be realized [17–19].

It should be mentioned that metals and semiconductors are distinguishable by the temperature-dependent electrical resistance. Whereas semiconductors do not conduct current at 0 K, the conductivity of metals increases more and more with decreasing temperature up to a point at which superconductivity sets in.

The third classification of solids represents insulators (e.g., diamond, ceramics). Here, the value of  $E_g$  is too high to be overcome by viable application of energy. No electrical conduction can be realized in these materials under practical conditions.

	AlN	GaN	GaAs	Si	InN	Ge
$E_g / eV$	6.2 [20]	3.4 [21]	$\sim 1.4 [14]$	$\sim 1.1 \ [14]$	$\sim 0.7$ [5]	$\sim\!0.7~[14]$
$E_g / nm$	200	365	$\sim 885$	$\sim 1130$	$\sim 1770$	$\sim 1770$

Table 2.2: Energy band gap  $E_g$  (T = 295 K) values of common semiconducting materials including group-III nitrides.

#### 2.2.2 n- and p-Type Doping

Impurities strongly affect the electronic and optical properties of semiconductors [7]. By intentional introduction of group-II or group-IV atoms into the GaN crystal lattice, additional holes or electrons are inserted into the material, respectively. Subsequently, the ability to conduct current is drastically increased. This concept is referred to as doping, namely n-type (group-IV, e.g., Si) and p-type (group-II, e.g., Mg). By bringing p-doped and n-doped GaN layers in contact to each other, a LED is created. The efficiency of the LED is further on drastically increased by insertion of a MQW consisting out of several alternating GaN and  $In_xGa_{1-x}N$  layers with nm-scale dimensions. As this in-depth technical background is not required to convey the results of this work, the reader may consult associated literature [7, 14–16, 22–24]. Today, GaN diodes with  $In_xGa_{1-x}N$  MQWs are the standard material system for the creation of blue and white LEDs. Versatile application is found in lighting, displays, consumer electronics, lasers, detectors and many more [5].

### 2.3 Metal Organic Chemical Vapor Deposition

In standard LED production, group-III nitrides are grown by epitaxial deposition. The concept of epitaxy is the growth of a material on top of a monocrystalline substrate surface, which can consist out of a different material. Thereby, the crystal lattice of the growth substrate is transferred to the grown material. In the case of a different substrate from the grown material (heteroepitaxy), the lattice mismatch between substrate and  $A^{III}N$  should be as small as possible to reach a high crystal quality. Most often, c-plane sapphire ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), silicon or 6H-SiC are used during GaN epitaxy [25]. Compared to that, during homoepitaxy both substrate and grown material are identical. It is applied in special cases for the growth of GaN layers with very high requirements in crystal quality, e.g., for lasers.

Next to substrate choice, different epitaxial methods exist depending on the intended material properties, e.g., molecular beam epitaxy (MBE), hydride vapor phase epitaxy (HVPE) and metal organic chemical vapor deposition (MOCVD) [26]. Out of these methods, the best LED performance is usually reached by MOCVD. Hereby, reaction of trimethyl aluminium (TMAI), trimethyl gallium (TMGa) or trimethyl indium (TMIn) with NH<sub>3</sub> occurs. The reactants are inserted into the MOCVD reactor in a carrier gas stream, which commonly is N<sub>2</sub> or H<sub>2</sub> (Figure 2.5, left). The substrate wafers are located on a rotating carrier under which a heater supplies a variable temperature of ~1000 °C. The whole system is kept at very low pressure around  $1 \cdot 10^{-7}$  Torr [27]. At a high temperature, the reactants form A<sup>III</sup>N on the substrate surface (Figure 2.5, right). Also, CH<sub>4</sub> is formed as a byproduct and removed from the reactor in an exhaust gas stream. By fine control over the partial pressure of every reactant gas, the composition of the epitaxial layer can be fine-tuned to reach the desired light wavelength. The molecular reaction occurs according to the following formula [19].

$$(CH_3)_3 A^{III} + NH_3 \rightarrow A^{III}N + 3 CH_4.$$

$$(2.7)$$

#### 2.3.1 Crystal Defects

In further discussions, the scope is restricted to GaN as it is the material system investigated during the course of this work. Sapphire has larger lattice constants than



Figure 2.5: Schematic overview of MOCVD reactor (left) [28]. From the left, gaseous reactants trimethyl-A<sup>III</sup> (TMA<sup>III</sup>) and NH<sub>3</sub> are inserted into the MOCVD reactor in a carrier gas stream of N<sub>2</sub> or H<sub>2</sub>. Epitaxial growth occurs on the heated sapphire substrate wafers. The byproducts of the reaction are carried away by the exhaust. Schematic epitaxial deposition of A<sup>III</sup>N from TMA<sup>III</sup> and NH<sub>3</sub> (right).

GaN (Table 2.3). This causes a general lattice mismatch of 33%. When GaN is deposited on c-plane sapphire, however, the lateral crystal orientation of GaN rotates itself by 30°. This leads to a reduced lattice mismatch of 13.8% in lateral direction [29]. The remaining mismatch still causes significant lateral strain in the growing GaN layer.

What adds to this intrinsic geometrical mismatch, is the difference in thermal expansion coefficients (Table 2.3). Whereas GaN growth is conducted at ~1000 °C, further processing and application of the LED is mostly under ambient conditions. The induced strain is partially reduced by disruption of the crystal lattice. This occurs in form of 0D-3D structural defects [31].

	GaN	$Al_2O_3$
a / Å	3.189[3]	4.758 [30]
c / Å	5.185[3]	12.99 [30]
$\alpha_0$ / K <sup>-1</sup>	$5.6 \cdot 10^{-6}$ [31]	$7.5 \cdot 10^{-6}$ [31]

Table 2.3: Lattice constants and thermal expansion coefficients of GaN and  $Al_2O_3$ . Due to the high temperature of ~1000 °C during epitaxial growth and further LED processing and operation at a lower temperature, additional strain is caused in the material.

#### 2.3.1.1 Zero-Dimensional Crystal Defects

Zero-dimensional crystal defects are also referred to as point defects. The crystal lattice is only interrupted in a single atom position. The main representatives are vacancies, interstitials and substitutional atoms (Figure 2.6). A vacancy describes an unoccupied position in the lattice. In case of an interstitial, an atom is additionally inserted into the crystal. A substitutional defect substitutes the correct atom. Depending on the type of atom associated with the point defect, intrinsic defects are caused by Ga or N atoms themselves. Thus, these represent vacancies, self-interstitials or antisites. At antisites, one species occupies the position of the other. Extrinsic defects, on the other hand, refer to foreign impurity atoms, which can form substitutional or interstitial impurities.



Figure 2.6: Schematic view of selected zero-dimensional defects in the gallium sublattice of a GaN single crystal [31].

#### 2.3.1.2 One-Dimensional Crystal Defects

1D crystal defects originate from a point defect during growth and evolve in a linear direction. The term threading dislocation (TD) thereby describes a perpendicular defect relatively to the substrate surface, which originates at the substrate and extends through the entire GaN layer. The Burgers vector  $\overrightarrow{b}$  characterizes the three classifications of TDs, which are edge, screw and mixed type dislocations (Table 2.4).

The Burgers vector  $\overrightarrow{b}$  can be understood by drawing an imaginary square around the dislocation termination site. One starts at a random atom surrounding the termination site and moves along the crystal lattice e.g., 3 atoms, whereby the dislocation line is passed. Further on, one moves the identical amount of atoms 90° relatively to the

Dislocation type	$\overrightarrow{b}$	Direction of $\overrightarrow{b}$ relatively to dislocation line
Edge	$\langle 11\overline{2}0\rangle$	90°
Screw	[0001]	0°
Mixed	e.g., $\frac{1}{3}\langle 11\overline{2}3\rangle$	$0^{\circ} < lpha < 90^{\circ}$

**Table 2.4:** Dislocation classifications and respective Burgers vectors  $\overrightarrow{b}$  [32].

initial direction and repeats this step twice. In case of no dislocation, one ends at the initial atom. If one step still has to be made to reach the initial atom, both direction and absolute value of this step are equivalent to  $\overrightarrow{b}$ . In case of a an edge dislocation,  $\overrightarrow{b}$  is perpendicular towards the propagation direction of the dislocation (Figure 2.7, left). On the contrary, screw type dislocations have a Burgers vector, which is parallel to the dislocation line (Figure 2.7, right). 1D dislocations with a  $0^{\circ} < \alpha < 90^{\circ}$  angle between  $\overrightarrow{b}$  and the propagation direction are referred to as mixed-type dislocations. Dislocations tend to follow the growth direction of GaN, which is mainly in z-direction perpendicularly to the substrate. Therefore, TDs generally span the entire epitaxial layer. If no strategy is applied for TD density reduction, it only decreases slightly with increasing GaN film thickness due to coalescence of individual TDs [33, 34].



**Figure 2.7:** Schematic view of edge (left) and screw type dislocations (right). The respective Burgers vectors  $\vec{b}$  are highlighted in red [31]. The Burgers vector of edge dislocations is perpendicular towards the dislocation propagation line. The Burgers vector of screw dislocations is parallel towards the dislocation line.

#### 2.3.1.3 Analysis of Threading Dislocation Density

At dislocation sites both the chemical stability and the electronic characteristics of the GaN layer are disturbed. On a Ga-polar epitaxial layer, treatment with hot alkaline solution showed etch pit formation at dislocation sites due to less resistance against etch erosion [35]. This concept will be further explained in chapter 3. The TD density can be determined by cathodoluminescence (CL) or photoluminescence (PL) microscopy from both polar crystal directions. In short, both methods will be referred to as CLM and PLM. The material hereby is irradiated with electrons (CLM) or above-band gap light (PLM). Simultaneously, the light emission of the excited material is detected. Dislocations act as centers of non-radiative recombination occurs. This leads to low light emission compared to intact crystal sections and therefore contrasts in the respective CLM and PLM images [36]. The reason for that is that non-radiative recombination competes with the radiative  $E_g$  emission and removes emission efficiency of the latter. This also anticipates why a high crystal quality is crucial for an efficient LED. For maximum internal quantum efficiency, the crystal quality must be as high as possible.

A third common technique for TD density evaluation is x-ray diffractometry (XRD) [37]. The peak width of a certain crystal reflex, e.g., (102), is evaluated. The higher the TD density is the more the observed reflex is broadened due to lattice distortion. This is quantified by the full width at half maximum (FWHM) value. In other words, the FWHM is the peak width in arcsec at half the maximum intensity [38].

Especially PLM and XRD will be later on applied in chapter 5 to characterize epitaxial layers used for the etch experiments. Both methods have individual advantages. PLM as well as CLM allow for direct counting of individual TDs in a certain section of the epitaxial layer. A further advantage represents that only dislocations are regarded that reach the MQW, provided that detected wavelength is chosen to be the intrinsic MQW emission. This is especially critical for the device performance of the finished LED. On the downside, only a microscopic section of the whole wafer is observed. Furthermore, aggregates of dislocations cannot be distinguished from single ones, which leads to a systematic underestimation error especially at high TD densities. XRD analysis, on the other hand, functions integral and allows for characterization of the entire GaN layer thickness. Information is thus obtained also about the underlying GaN layers.

values can be compared very well. For that, a comparable film thickness and identical measurement parameters are a necessity.

#### 2.3.1.4 Other Types of Crystal Defects

Two-dimensional defects represent an interface between two single-crystalline regions of the epitaxial layer that have different crystal orientations. Examples for 2D defects are grain boundaries or inversion domains, latter of which can be a transition from Ga- to N-polarity of c-plane GaN. Finally, 3D defects in the crystal lattice are mostly macroscopic and originate e.g., from an overgrown particle. Voids or cracks in the epitaxial layer are examples for these.

#### 2.3.2 Strategies for Dislocation Density Reduction

During MOCVD growth of GaN directly on c-plane sapphire, the TD density is in a range of  $10^{10}$  cm<sup>-2</sup> [39, 40]. TDs are detrimental for device performance. As stated above, they act as centers for non-radiative recombination. Also, they negatively influence electron mobility. Both phenomena decrease efficiency. In addition to that, the generated electrical resistance causes heating up of the device, which effectively lowers its life time [41, 42].

#### 2.3.2.1 AIN and GaN Nucleation Layers

The mismatch between the lattice parameters of sapphire and GaN is a major reason for the development of a high TD density. To address this issue, a GaN or AlN nucleation layer is commonly grown on the sapphire substrate prior [43]. This accomodates the lattice mismatch and enables a lower TD density in subsequently grown GaN layers [44, 45]. Also, it allows for control over the crystal polarity, which is of utmost importance for device manufacturing [11, 46, 47]. By nucleation layer growth, the TD density could be decreased to a value of ~ $4 \cdot 10^8$  cm<sup>-2</sup> [48].

#### 2.3.2.2 Change of Growth Direction

Another strategy for effective TD density reduction is the temporary change of growth direction during epitaxy. Dislocations tend to follow the growth direction. As soon as 3D growth is initiated, the dislocations are partially bent into lateral direction and terminate to a large extent.

To accomplish this, a silicon nitride  $(SiN_x)$  interlayer can be *in situ* grown on top of the GaN surface directly in the epitaxy reactor [49, 50].  $SiN_x$  is hereby deposited with a layer thickness lower than a single-atomic layer. Thus, it only partially covers the GaN surface. When in the next epitaxial step GaN growth continues, it only does so in surface regions not covered by  $SiN_x$ . This leads to GaN island formation. The GaN islands coalesce in lateral direction as GaN growth continues. In Figure 2.8, left, the lower epitaxial layer was grown in z-direction, which is visible by the vertical TD lines. After the inserted  $SiN_x$  layer, the growth direction had a ~60° angle towards the substrate. Dislocations followed the growth direction and were bent into lateral direction. On the left side of Figure 2.8, left, still surface sections can be seen in which GaN growth further occurred in z-direction. In these sections, no  $SiN_x$  was present on top of GaN. Thus, no TD bending occurred. With this approach of a changed growth direction, a dislocation density of  $9 \cdot 10^7 \text{ cm}^{-2}$  was reached.

Next to  $SiN_x$  deposition, also a pressure change in the MOCVD reactor can control the growth direction of GaN [52]. Nucleation layer growth at low reactor pressure leads to island formation and quick coalescence. By raising the reactor pressure, the coalescence in lateral direction can be enhanced leading to a lower number of generated coalescence dislocations.

#### 2.3.2.3 Patterned Sapphire Substrates

Compared to the conventional c-plane sapphire substrates, patterned sapphire substrates (PSS) employ a periodic array of nm- to µm-scale surface features (Figure 2.9, top left) [53]. These are prepared by wet- or dry-chemical etching and function in the same way as GaN island growth and coalescence after  $SiN_x$  deposition.

Commonly, PSS features are plateaus with angled side facets. On the bottom c-plane sapphire, initial GaN growth occurs preferably (Figure 2.9, top right) [54]. By control


Figure 2.8: Cross section TEM image of GaN layer with in situ deposited SiN<sub>x</sub> layer for TD density reduction (left). Island formation is visible in form of a clear contrast between 2D GaN (bottom) and coalescing 3D grown islands (top). Thereby, TDs proceed in vertical direction in 2D GaN. In the 3D GaN islands, the direction of TDs has a lateral component (i.e., TD bending). Reproduced with permission. Copyright 2007, Elsevier [49]. Cross section TEM images of dislocation bending by GaN growth on patterned sapphire substrates (PSS) (right). Directly over the angled sapphire side walls (white 45° sections) TDs have a lateral direction. Due to that, the local TD density has its lowest value directly above angled PSS sidewalls. Adapted with permission. Copyright 2007, American Institute of Physics [51].

over the growth conditions, a lateral growth component of the emerging GaN islands is produced. The coalescence of the latter occurs directly over the angled side facets of the PSS, on which no GaN was deposited (Figure 2.9, bottom right). This leads to dislocation bending. The reduction in TD density thus is locally directly dependent on the distribution of PSS features, which was confirmed by TEM analysis and etching (Figure 2.8, right) [51, 55]. This local variation in TD density will pay a role in subsection 3.2.2. As an additional positive effect on the light extraction efficiency of the chip, the PSS patterns function as a reflective interface. If the substrate remains a part of the finished chip design, this leads to more efficient light outcoupling.

Next to the presented methods for TD density reduction, other techniques exist including epitaxial lateral overgrowth. These are not discussed here [56].

2 Properties of Group-III Nitrides



Figure 2.9: Schematic overview of GaN growth on PSS substrates; substrate before growth (top left); initial growth, which occurs at higher rate on the bottom features (top right); island growth (bottom left); coalescence (bottom right). The TD density is particularly low over the angled PSS features due to dislocation bending in these positions (compare to Figure 2.8, right) [54].

# 2.4 Flip-Chip LED Processing

For the design and production of highly efficient GaN LEDs, the sapphire substrate used during epitaxy entails intrinsic problems [57]. Firstly, the undirected emission of photons costs device efficiency. The reason for that is that photons also shine towards and penetrate the translucent sapphire substrate. Thus, these photons do not take part in usable light output. This is especially an issue in many common singledirectional applications as e.g., traffic lights or LCD displays. Secondly, sapphire has a low thermal conductivity. Heat dissipation is not effective and lowers the maximum operating current due to device overheating. Both these disadvantages can be overcome by exchanging the sapphire substrate by a silicon carrier. This concept of transferring the epitaxial GaN layer from sapphire onto a different substrate is referred to as flipchip technology (Figure 2.10) [58]. The epitaxial layer is "flipped" by bonding the new substrate onto the top side of the GaN layer and removing the initial sapphire growth substrate.



Figure 2.10: Schematic cross sections of a conventional LED chip on a sapphire substrate (left) and a flip-chip LED bonded onto a silicon substrate (right). Notice that the order of p-GaN, MQW and n-GaN is reversed [57].

The most significant steps during flip-chip processing are shown in Figure 2.11. After the initial epitaxial GaN growth, a lot metal layer is applied on top of p-GaN. This combines efficient photon reflection to the chip surface with the necessary adhesive interface between p-GaN and the silicon carrier. The latter is solder-bonded onto the lot metal in the next step followed by LLO to remove the sapphire substrate.

LLO employs laser light irradiation on the sapphire side of the LED wafer [59, 60]. Hereby, the laser light wavelength is chosen in between  $E_g$  (GaN) and  $E_g$  (Al<sub>2</sub>O<sub>3</sub>), which leads to light absorption in the most substrate-near GaN layer. Beforehand, the laser light can shine through the sapphire substrate almost without hindrance. As GaN is decomposed by the induced heat, metallic Ga and gaseous nitrogen form [61]. Especially nitrogen gas formation applies sufficient pressure to the GaN-sapphire interface to separate both layers. If an AlN nucleation layer was deposited prior to epitaxial GaN growth, the laser light also shines through AlN due to the higher  $E_g$  (AlN) compared to  $E_g$  (GaN).

After LLO, wet-chemical etching - the key part of this work - is applied. Thereby, a rough n-GaN surface is created. Side-wall etching describes the separation of the entire epitaxial stack in vertical direction to form electrically separated LEDs. Also, the GaN surface is passivated for resistance against changing environmental conditions, which the finished product will face. The metal contact pads are deposited to enable solder bonding of electrical wires. After backside metallization and chip separation, the individual LEDs are attached onto a ceramic carrier and molded into a silicone

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matrix. Commonly, the latter features a lens design for controlling the requested light shine characteristics of the LED. The wet-chemical etch process of GaN is emphasized by the black frame in Figure 2.11 and will be discussed in the following chapters.



Figure 2.11: Schematic main steps of flip-chip LED process flow. The wet-chemical etching of GaN to produce a rough surface is highlighted in a black frame. Reproduced with permission. Copyright 2018, Wiley VCH [62].

# 3 Wet-Chemical Etching of Gallium Nitride

# 3.1 Improvement of Light Extraction Efficiency

Two important parameters describing the efficiency of a LED chip are internal and external quantum efficiency [63]. The former represents the number of photons generated by a certain amount of current flowing through the semiconductor device. It is mainly enhanced by crystal quality improvement [64]. The external quantum efficiency corresponds to the percentage of generated photons which can leave the chip to take part in lighting. Light outcoupling from the chip is critically influenced by the interface between GaN and air. The refractive indices of GaN and air are  $n \approx 2.5$  and n = 1.0, respectively [65]. This leads to a light escape cone with a value of only 23.6°. If a photon is emitted inside this escape cone, it can cross the interface and take part in the luminance of the LED [66, 67]. However, generated photons in the MQW are emitted into random directions. Most of them undergo total internal reflection at the smooth GaN-air interface. Subsequently they are either absorbed at the chip edge or escape through the chip sidewalls (Figure 3.1, left) [68].

If the N-face of GaN, which is revealed by LLO, is immersed in alkaline aq. solution, an anisotropic etch process takes place. Anisotropic means that different crystal orientations are etched more or less quickly. In case of GaN, based on the hexagonal crystal lattice, hexagonal pyramids evolve on the N-polar surface (Figure 3.1, right). By pyramid development, both the total surface area and the number of surface angles are significantly increased. This leads to up to a fourfold improvement in light extraction efficiency [69]. Photons that were initially directed outside of the escape cone can be redirected back into the escape cone at the diffuse surface (Figure 3.1, center).



Figure 3.1: Schematic emission pathway of a photon which was generated outside of the 23.6° light escape cone without (left) and with surface roughening (center). The pyramidal surface of the roughened chip obtains significantly more possibilities for generated photons to be emitted instead of internally reflected. Adapted with permission. Copyright 2018, Wiley VCH [62]. 45° scanning electron microscopy (SEM) image of N-polar GaN surface after 6 min etching in 30 wt. % aq. KOH at 80 °C (right). A dense array of hexagonal pyramids is visible.

Parish and his group [70] reported GaN etching in molten alkali metal salts at temperatures up to 800 °C. Also, bulk and heteroepitaxial GaN was etched slowly in highly concentrated aq. NaOH, KOH and  $H_3PO_4$  solutions [71–74]. The temperature was hereby chosen between 80 and 130 °C. At RT, no etch progress was found [75]. Due to the high stability of GaN against wet-chemical etching, a lot of effort was put into the development of dry-chemical etch approaches, e.g., inductively coupled plasma (ICP) etching or reactive ion etching (RIE) [76].

Compared to dry-chemical methods, however, wet-chemical etching has several advantages. First, it creates clean, smooth and straight crystal facets. Surface damage in form of undefined bonds and decomposition materials was not found on the surface due to superior solubility of the latter compared to monocrystalline GaN [77]. Wet-chemical etching was used by Itoh and co-workers [78] to effectively remove surface damage induced by foregoing dry-chemical etching. Secondly, a better optical and electrical performance in terms of hall mobility after wet-chemical etching was reported.

# 3.2 Material-Dependent Influences on Etch Pattern and Rate

A variety of influences on the GaN ER and developing surface has been reported. These can be separated into material- and process-dependent ones. The most important influences are summarized in Figure 3.2 [62].



Figure 3.2: Summary of main influences on GaN ER in aq. alkaline solution as reported in literature. The font size indicates the relative impact of each influence. Adapted with permission. Copyright 2018, Wiley VCH [62].

#### 3.2.1 Growth Conditions and Resulting Crystal Polarity

As one of the first impacts on the etch success of GaN, the growth conditions during epitaxy were reported. These represent presumably the most important influence as well. Weyher and co-workers [73] performed GaN etching in 5-40 wt. % aq. KOH and NaOH solutions. Epitaxial GaN samples that showed a smooth surface prior to etching were not eroded at all. In the case of bulk single crystalline GaN, only one crystal facet was attacked at a maximum ER of 22 nm min<sup>-1</sup> (~20 wt. % KOH). After a short etch

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time, pyramids were found scatteredly on the otherwise flat GaN surface. After 10 min etching, the entire sample surface was covered with pyramids. Later on, Carosella and co-workers [79] performed etch experiments with samples grown by different epitaxial techniques. Both at RT and 80 °C, neither MOCVD nor HVPE samples were etched in the common AZ-400 K photoresist developer solution. The latter contains KOH as the active species. Only MBE grown GaN was etched. Li and his group [80] further added hot wall epitaxy (HWE) to their investigations. Moreover, multiple combinations of nucleation layers and epitaxial layers were created by variation of the growth techniques (Table 3.1).

No correlation was observed between successful etching and the foregoing surface morphology. The critical parameter was found to be the crystal polarity of GaN, which itself was controlled by the nucleation layer. While Ga-polar epitaxial layers were highly stable against etching, N-polar layers showed etch removal combined with development of hexagonal pyramids. The polarity also explains the observed etch behavior of bulk single-crystalline GaN, which only showed material removal on one facet of the crystal [73].

AlN nucleation layers with different thicknesses were investigated by Palacios and coworkers [81]. Samples I comprised a 10-20 nm AlN layer, whereas samples II were prepared with 30-50 nm AlN prior to GaN growth. The GaN polarity was detected to be N-polar (I) and Ga-polar (II). Only I could successfully be etched regardless of KOH concentration, etch time and solution temperature.

Ng and co-workers [47] reported the growth of Ga- and N-polar GaN adjacent to each

Epitaxy technique	Surface morphology	Successful Etching
MOCVD	Smooth	No
MOCVD	Smooth with hexagonal features	Etched
MOCVD on HVPE GaN	$\operatorname{Smooth}$	No
MOCVD on MBE GaN	Rough	Etched
HVPE	Rough	No
MBE	Rough	Etched
HW on HVPE GaN	Rough	No
HW on MBE GaN	$\operatorname{Smooth}$	Etched

Table 3.1: Etching results of different combinations of epitaxial growth conditions reported by Li and co-workers. Adapted with permission. Copyright 2000, Wiley VCH [80]. other on the same wafer. First, a 20-30 nm thick AlN nucleation layer was deposited at 720 °C followed by ~100 nm GaN to prevent oxidation of AlN. The polarity of this GaN layer was determined to be Ga-polar. After partially covering the surface, open AlN/GaN was removed by RIE/ICP etching with a Cl/Ar gas mixture. Hereby, the underlying sapphire substrate was revealed. Further on, GaN was epitaxially grown on the pretreated substrate. Regions with AlN/GaN nucleation layer yielded a smooth Ga-polar GaN surface, whereas on the blank sapphire substrate N-polar GaN was grown. This was clearly visible after subsequent etching in 10 wt. % aq. KOH at 90 °C (Figure 3.3). N-polar regions showed the characteristic pyramidal morphology, whereas Ga-polar material was not attacked.



Figure 3.3: 45° SEM image of GaN surface with alternating Ga- and N-polarity after 45 min etching in ~ 10 wt. % aq. KOH at 90 °C. The flat GaN stripes were grown in Ga-polar direction so that no etch attack occurred. The rough pyramidal surface sections were grown in N-polar direction and subsequently etched by KOH. Reproduced with permission. Copyright 2003, American Institute of Physics [47].

Next to nucleation layer growth, Seelmann-Eggebert and his group [11] reported that substrate nitridation effectively controls the developing GaN polarity. Sapphire substrates were exposed to NH<sub>3</sub> at 1100 °C for 1-3 min [46]. At a NH<sub>3</sub> partial pressure of  $\sim 10^{-5}$  bar, AlN islands were formed with a thickness of 20-30 Å. The water pressure at the sapphire interface was kept lower than 10<sup>-6</sup> bar. The equilibrium of the following reaction, which at ambient conditions is thermodynamically unfavorable, was thus shifted to the right side of the following equation.

$$Al_2O_3 + 2 NH_3 \rightleftharpoons 2 AlN + 3 H_2O \tag{3.1}$$

GaN growth above AlN islands occurred N-polar. With all NH<sub>3</sub> traces removed from the epitaxy reactor, smooth Ga-polar layers were obtained.

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Substrate nitridation combined with carrier gas variation between  $H_2$  and  $N_2$  was investigated by Yamamoto and co-workers [82]. Substrate nitridation was carried out at 900 °C for 30 min. In comparison to the study of Seelmann-Eggebert, a lower temperature was applied. This was compensated by a longer process time. Subsequently, a 40 nm thick GaN buffer layer was grown followed by the actual epitaxial GaN growth. The surface of nitrided samples was characterized by scanning electron microscopy (SEM) before and after etching in 6 wt. % aq. KOH solution for 20 min (Figure 3.4). Both before and after etching, GaN grown on nitrided substrates in combination with  $H_2$  carrier gas showed a smooth surface. The use of  $N_2$  carrier gas led to a higher number of circular pits, which remained unchanged after etching. A slow ER in both cases (2- $5 \,\mathrm{nm\,min^{-1}}$ ) led to the conclusion that both samples had Ga-polarity. Samples grown without foregoing substrate nitridation resulted in a significantly higher pit density. The combination of  $N_2$  carrier gas with no substrate nitridation could not yield singlecrystalline GaN at all. Etching of non nitrided samples was performed in 7 wt. % aq. KOH for 20 min. The observed ER was higher with values up to 100 nm min<sup>-1</sup>. Thus, N-polarity was suggested. However, this conclusion disagrees with the experimental results reported by Seelmann-Eggebert [11]. The smooth morphology after etching gives evidence to Ga-polarity. N-polarity of the layer should have developed a pyramidal surface during etching. The high ER was most likely caused by the high density of µm-scale crystal errors, which subjected multiple other crystal facets besides the lateral Ga-face to the KOH solution.

In summary, polarity control was achieved by the choice of the epitaxial growth technique, nucleation layer growth or substrate nitridation. N-polar samples were found to be etched at a reasonable rate and under pyramid formation. Etching of Ga-polar material was only possible in case of a poor crystal quality [46, 65, 82, 83].

#### 3.2.2 Intrinsic Crystal Defects

Dislocations formed due to lattice mismatch and growth imperfections were reported to have a strong impact on the wet-chemical etching of GaN. Han and his group [84] immersed Ga-polar samples in 13 wt. % aq. KOH at 80 °C for 10 min for the determination of the TD density. Application of a thin  $SiN_x$  nucleation layer and H<sub>2</sub> carrier gas during epitaxial growth afforded a TD density of ~3 · 10<sup>-9</sup> cm<sup>-2</sup>. After etching, by atomic force microscopy (AFM) and topological profiling, etch pits of three different



Figure 3.4: SEM images of MOCVD grown GaN samples on nitrided sapphire substrates with H<sub>2</sub> carrier gas before (a) and after (b) etching for 20 min in boiling 6 wt. % aq. KOH solution; with N<sub>2</sub> carrier gas before (c) and after (d) etching. SEM images of MOCVD grown GaN samples on blank sapphire substrates with H<sub>2</sub> carrier gas before (e) and after 1 min (f), 5 min (g) and 10 min (h) etching in boiling 7 wt. % aq. KOH solution. The scale bar is identical for all images. Adapted with permission. Copyright 2002, Wiley VCH [82].

TD types could be distinguished. Screw-type TDs appeared on or at the end of steps of a terrace-like surface morphology. Mixed-type TDs were observed exclusively at the end of these steps. Edge-type TDs were found as etch pits on the flat terraces. GaN directly surrounding a dislocation was dissolved at a higher rate, which was attributed to increased strain associated with TDs relatively to perfect single-crystalline material [85]. This initial etch attack in an otherwise stable material was also reported by Han and co-workers [35]. Due to a higher ER in lateral compared to vertical direction, development of terraces parallel to the surface is feasible. Also the presence of point defects was proposed to cause the formation of etch pits [86]. In case of Ga-face etching, it can be concluded that crystal defects enable an etch attack by aq. KOH, which does not take place in case of perfect single crystals.

In the case of N-face GaN, no preferential etch direction was observed along defects or surface irregularities [81]. The formed pyramids were predominantly monocrystalline, however. This suggested that crystal regions containing dislocations were etched faster.

Chang and co-workers [87] prepared GaN samples on PSS substrates followed by LLO to reveal the N-face of GaN. Before etching, the PSS features appeared as circular cavities on the surface. After 10 s, 20 s, 60 s and 120 s etching in 140 °C KOH solution, SEM analysis showed a volcano like crater structure on the surface (Figure 3.5). The

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Figure 3.5: SEM images of GaN samples grown by MOCVD on PSS and lifted by LLO. Surface directly after LLO (top left) and after 10s (top center), 20s (top right), 60s (bottom left and center) and 120s etching in 140 °C KOH solution. On top of the PSS sidewalls in between A and B, crater ridges were formed as a consequence of less etch removal compared to A and B. This was attributed to a lower relative dislocation density. Adapted with permission. Copyright 2012, Wiley VCH [87].

characteristic dislocation distribution caused by PSS growth directly correlated with the ER. In the middle of protruding areas  $\mathbf{A}$  as well as in the middle of circular cavities  $\mathbf{B}$ , the dislocation density and also the ER was the highest (Figure 3.5, top left). Directly over the PSS sidewalls, where the dislocation density had a minimum, less etch removal led to the formation of circular crater ridges [55]. These craters were most pronounced after 60 s etching. After 120 s etching, the crater ridges were eroded as well leading to pyramid formation on top of the craters. As a consequence, etching of N-face GaN was claimed to be accelerated by a high number of dislocations. As from the N-side also single crystalline material can be etched, however, the selectivity between intact and defective crystal regions is not as high as it is the case for Ga-face GaN. That crystal defects are preferentially removed from the N-face by wet-chemical etching also was reported after observation of superior PL characteristics and thus an improved crystal quality achieved by etching [81, 88]. The ER dependence on the density and individual positions of TDs will be discussed in detail later on in chapter 5.

#### 3.2.3 Compositional Variation in Al<sub>x</sub>Ga<sub>1-x</sub>N

N-polar  $Al_{0.12}Ga_{0.88}N$  grown on Si(111) showed a ~30% increase in ER relatively to GaN when immersed in 31 wt.% aq. KOH at 40 °C [81]. Linear correlation between the ER and  $Al_xGa_{1-x}N$  composition was observed, whereby AlN had a 12:1 selectivity against GaN [89]. This trend seems to be independent from etch conditions as both groups employed a different etch process. Ga-face  $Al_{0.12}Ga_{0.88}N$  was not etched at all.

#### 3.2.4 Doping and Conductivity

N- or p-doping influences both structural and electronic properties of GaN. By Mgdoping, a twofold enhancement in lateral p-type conduction was reported as well as a fivefold increase in vertical conduction [90]. Also the dislocation density was reduced by about one order in magnitude, which implied an influence on the ER. For Ga-face material, however, no influence of carrier concentration and electron mobility on the ER was found [79]. Quantitative results were published for 85 wt. % H<sub>3</sub>PO<sub>4</sub> etching of Ga-face GaN at 190 °C [72]. Etch pits appeared in higher number and larger size in material with very a high carrier concentration of  $10^{19} - 10^{20}$  cm<sup>-3</sup>. When the carrier concentration was reduced to  $10^{18}$  cm<sup>-3</sup>, the pit density was decreased from  $10^7$  cm<sup>-2</sup> to  $3 \cdot 10^4$  cm<sup>-2</sup>. As next to carrier concentration also other parameters like strain and dislocation density vary with growth conditions, a clear correlation has not yet been found, especially for N-face GaN.

# 3.3 Process-Dependent Influences on Etch Behavior

In most cases, material-dependent influences are difficult to control due to a dense network of interactions between etching and the multiple foregoing processes. For example, conductivity and electrical connection of the epitaxy are designed for specific chip characteristics and cannot be easily adapted to the demand of surface roughening. Also, the dislocation density generally has the lowest value possible to maximize the performance of the chip. On the other hand, process-dependent parameters like KOH concentration, solution temperature and etch time are direct and controllable variables. In the following, the ER dependency on each of these variables is reviewed.

#### 3.3.1 KOH Concentration

From  $\sim 3-23$  wt. % aq. KOH, MBE grown GaN showed a linear increase in ER with KOH concentration at 40 °C [81]. The ER maximum was found at 27 wt. % aq. KOH. Higher concentrations led to a rapid decrease in ER. At 31 wt. % aq. KOH, the ER only reached half the value that had been determined at 27 wt. %. The same curve shape was found at 80 °C solution temperature. The ER increase between  $\sim 3$  and 27 wt. % aq. KOH was attributed to the increasing availability of OH<sup>-</sup> ions. The ER decrease found for high KOH concentrations was ascribed to diffusion limitation, which is feasible due to high density and viscosity of the solution. Similar correlations were reported for etching in phosphoric acid and under photoelectrochemical (PEC) conditions [91]. Also, during etching in KOH-ethylene glycol solution at 170 °C, the maximum ER was found at 40 wt. % KOH. With a further increase to 50 wt. % KOH, the ER dropped significantly.

#### 3.3.2 Solution Agitation

Solution agitation generally impacts the reaction rate of diffusion limited reactions. By sufficient convection, a local shortage of reactive species is circumvented, which increases the ER. In the case of GaN etching, this case equals a shortage of  $OH^-$  ions at the GaN-solution interface. During N-polar GaN etching under dark and electroless conditions, stirring frequencies of 0, 250, 500 and 750 rpm were applied [81]. All experiments yielded an identical ER regardless of stirring frequency. Also, ultrasonic treatment had no influence on the reaction kinetics. Without light and bias voltage application, GaN etching thus is not diffusion limited. In the case of PEC etching of  $In_xGa_{1-x}N$ , diffusion limitation was reported [92]. Harush and co-workers [93] observed etch profile differences for varying stirring velocities as well at ER values as high as 1 µm min<sup>-1</sup>. In these experiments, GaN was masked with 150 µm wide Ti:Al:Ni:Au metal layer stripes. Nearby the metal stripes faster etching was observed. However, next to material transport, also conductivity and charge distribution effects become more important at very high ER values. At the lower ER achieved during common dark and electroless etching, agitation can be neglected according to foregoing literature.

#### 3.3.3 Etch Time and Temperature

Palacios and co-workers [81] varied the KOH solution temperature in a range of 25 °C-80 °C. At any temperature, linear etching was observed over a period of 50 min, after which the process was disrupted. Linear etching was found independently from KOH concentration. Formation of a passivation layer was therefore not the case under normal conditions. The material removal depended linearly on etch time.

For different KOH solution temperatures, an exponential increase in ER was reported. Compared to a N-polar GaN ER of ~ 2 nm min<sup>-1</sup> at 40 °C, the ER increased to 50 nm min<sup>-1</sup> at 80 °C. This 25-times higher value agrees with the results published by Wang and co-workers [94]. The activation energy  $E_a$  of the reaction was determined by several groups via plotting the ln (ER) against  $T^{-1}$  and fitting the Arrhenius equation [95].

$$k = A \cdot e^{-\frac{E_a}{k_B T}} \tag{3.2}$$

Hereby, k is the rate constant, A is a reaction-specific constant pre-exponential factor,  $E_a$  is the activation energy,  $k_B$  is the Boltzmann constant and T the absolute temperature (in K).  $E_a$  values ranging from 0.13 eV to 0.78 eV were reported [35, 47, 81, 94]. In summary, etching depended linearly on etch time and exponentially on solution temperature.

#### 3.3.4 Surface Damage Induced by Preprocessing

An accelerated ER was also observed in the case of crystal damage induced by preprocessing. Irradiation of N-face GaN with KrF laser light led to photothermal etching and photoablation [96]. The  $GaO_x$ -GaN residues formed at irradiated sites were easily removed by HCl-HF treatment to achieve surface structuring. Afterwards, 27 wt. % KOH etching at 60 °C yielded an uniform pyramid coverage.

Also, B<sup>+</sup> and Ar<sup>+</sup> ion-implantation of Ga-polar material was conducted [79]. Up to the implanted material depth, etch removal during subsequent KOH treatment was generated. Non ion-implanted sections, on the other hand, were not eroded at all. Au<sup>+</sup> implantation with doses  $\geq 5 \cdot 10^{15}$  ions cm<sup>-2</sup> enhanced pit formation during subsequent etching of Ga-polar GaN [97]. The development of individual pits was, however, not caused by implantation of individual ions. The pit density was several orders of

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magnitude lower than the implantation dose. Gold implantation was combined with  $SiO_2$  masking of the GaN surface [98]. After mask removal, 10 wt. % aq. KOH etching at 80 °C for 20 min resulted in trenches located at implanted positions.

Also dry-chemical etching can be understood as surface damage prior to KOH etching. Material residues caused by plasma etching were successfully removed by subsequent wet etching [99]. Thereby, surface leakage currents were reduced proving superior surface quality.

# 3.4 Etch Mechanism on Atomic Scale

#### 3.4.1 Molecular Reaction Mechanism

The molecular etch mechanism of GaN has been reported controversially. In general, the etch progress was suggested to be a combination of oxidation and dissolution [100]. Dissolution is thereby accomplished by the alkaline solution at elevated temperature. Two alternatives for initial oxidation were reported. Li and co-workers [83] proposed formation of  $Ga_2O_3$  and  $NH_3$  according to the following formula.

$$2 \operatorname{GaN} + 3 \operatorname{H}_2 O \rightarrow \operatorname{Ga}_2 O_3 + 2 \operatorname{NH}_3$$

$$(3.3)$$

By X-ray photo electron spectroscopy (XPS), the presence of Ga-O and Ga-OH bonds were detected on both Ga- and N-polar GaN. This led to the suggestion that hydroxide ions are adsorbed to the surface and form gallium oxide via Ga oxidation. KOH was thereby reported to act as a catalyst [101]. A N-H<sub>3</sub> peak gave evidence that ammonia is formed during the etch reaction. The oxygen peak on the surface after etching was smaller than before. Formed gallium-oxygen species were thus quickly dissolved under the strongly alkaline conditions. As an intermediate step, Guo and co-workers [89] reported the formation of  $Ga(OH)_3$  according to the following mechanism.

$$GaN + 3 H_2O \rightarrow Ga(OH)_3 + NH_3$$

$$(3.4)$$

The above presented mechanistic approaches both have no evident electronic influence on the ER. In contrast, other studies base on an electrochemical etch process. This requires the presence and transport of electrons and holes and is in the context of anodic dissolution, which takes place in case of other semiconductor compounds [102, 103].

$$2 \text{ GaN} + 6 h^+ \rightarrow 2 \text{ Ga}^{3+} + \text{N}_2$$
 (3.5)

$$6 \text{ H}^+ + 6 e^- \rightarrow 3 \text{ H}_2$$
 (3.6)

GaN oxidation hereby consists out of a combination of two electrochemical reactions. The main difference to the above reported mechanisms is that nitrogen and hydrogen gas are formed rather than NH<sub>3</sub>. The electron transport was suggested by Wang and co-workers [94] to occur in four steps. These are (I) excitation of the electron from the Fermi level  $E_F$  to the conduction band  $E_{CB}$  and (II) migration to the GaN-solution interface. Steps (III) and (IV) represent spatial combination and reaction with the oxidizer H<sup>+</sup>. Thereby, steps (II) and (III) were proposed as rate-determining. Step (II) was suggested to have two important components, i.e., the thermal emission-diffusion limited  $I_{TE,D}$  and the electron tunneling component  $I_T$ . Whereas  $I_{TE,D}$  depends on temperature, electron tunneling is provided by crystal defects. The mainly diffusion-controlled step (III) brings conductivity and KOH concentration, into effect. Assuming perfect material quality with no electron tunneling, an ER increase following a solution temperature increase from  $T_1 = 60$  °C to  $T_2 = 90$  °C was expressed theoretically as

$$\frac{\text{ER}(T_2)}{\text{ER}(T_1)} \approx \frac{\sqrt{T_2} \ e^{\frac{-\Delta\Phi}{k_b T_2}}}{\sqrt{T_1} \ e^{\frac{-\Delta\Phi}{k_b T_1}}} \approx \frac{\sqrt{363} \ e^{-25.284}}{\sqrt{333} \ e^{-23.20}} \approx 7.71 \quad . \tag{3.7}$$

Hereby,  $\Delta \Phi$  is the potential barrier height between  $E_F$  and  $E_{CB}$  directly at the GaNsolution interface. For  $\Delta \Phi$ , a theoretical value of 0.73 eV was calculated. The experimentally observed activation energy  $E_a = 0.78 \text{ eV}$  was in good agreement with that. An experimental temperature increase from 60 °C to 90 °C, however, only led to an ER increase of factor ~3 instead of the calculated 7.71.  $I_T$  was attributed to be the reason for that as it is mainly influenced by the intrinsic dislocation density, which is independent from temperature. KOH concentration was considered to mainly impact steps (II) and (III). A concentration decrease not only complicates electron trespassing from GaN to solution but also decreases catalytic activity during Ga oxidation as well as Ga<sup>3+</sup> solubility. GaN etching was assumed to be kinetically controlled over a wide KOH concentrational range. Diffusion limitation was suggested to only play a role at

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very small KOH concentrations of  $0.01 - 0.1 \text{ mol } \text{L}^{-1}$ .

Diffusion limitation in  $0.04 \text{ mol } \text{L}^{-1}$  aq. KOH was indeed reported by Youtsey and coworkers [103] under PEC conditions. In unstirred solution, the ER of Ga-polar n-GaN saturated earlier for high illumination intensities above  $20 \text{ mW cm}^{-2}$ . In stirred solution, on the other hand, the ER increase remained linear with light illumination intensities up to  $50 \text{ mW cm}^{-2}$ . The diffusion limitation in unstirred solution was explained by the induction of enough photo-generated electron-hole pairs to shift kinetical hindrance towards mass transport limitation.

Both the electroless and electrochemical mechanistic approaches appear plausible. It has already been shown that the process conditions during etching influence the occurring reaction. Under PEC conditions, several more mechanisms comprising formation of  $N_2$  and  $H_2$  have been reported [104, 105]. In conclusion of all reported mechanisms, hydroxide ions initially attack Ga back bonds leading to formation of gallium-oxygen species. The latter are subsequently dissolved in alkaline solution. The molecular etch reaction occurring under dark and electroless conditions will be investigated and discussed in chapter 8.

#### 3.4.2 Directional Etch Anisotropy

Next to the stoichiometric etch reaction, the root cause for anisotropic etching has been discussed in foregoing literature as well. Hydroxide attack on Ga, which was found to be the first step of etching, depends on the crystal lattice geometry due to steric and electronic hindrance [83, 106, 107]. From SEM images, the angles of both pyramid and etch pit side walls during etching of N-face and Ga-face material relatively to the  $(000\overline{1})$  plane were reported to be ~ 60° [35, 47, 81]. Palacios and co-workers [81] assumed pyramid side planes to be {11 $\overline{2}1$ } crystal facets. However, several later reports concluded that {10 $\overline{11}$ } crystal facets make up the pyramid side planes. The theoretical angle relatively to the -c horizontal plane has a value of 62.1° being in good agreement with the experimentally obtained value of ~60°. The anisotropic etch behavior will be also discussed in chapter 8. Hereby, the previously reported data will be associated with the experimental results for the development of a comprehensive model.

# 4 Materials and Methods

After the presentation and in-depth discussion of the state of knowledge prior to this work, in this chapter, the applied materials and methods are explained. The used chemicals as well as GaN sample materials are described. Also, analytical methods for the characterization of the material and surface properties are presented. Two important key parts of this work, i.e., the ICP-OES analysis of the etch kinetics as well as the white light interferometry (WLI) analysis of the roughness homogeneity, are explained in detail.

### 4.1 Materials

#### 4.1.1 Chemicals

KOH was purchased from BASF as Selectipur grade. Carl Roth supplied 36 wt. % pro analysi (p.a.) grade HCl and 36 wt. % p.a. grade HNO<sub>3</sub> for ICP-OES sample preparation. Ar and NH<sub>3</sub> were bought from Linde Electronics GmbH & Co. KG in liquid form. (CH<sub>3</sub>)<sub>3</sub>Ga and (CH<sub>3</sub>)<sub>3</sub>Al were purchased from Nata Opto Electronic Material Co. Buffered oxide etch (BOE) solution was received from Honeywell with 4.15 wt. % HF and 33 wt. % NH<sub>4</sub>F. No surfactants and additives were contained in BOE solution. NaOCl (14 wt. % active Cl<sub>2</sub> in aq. solution) was received from VWR as GPR Rectapur grade. Thymol was bought from VWR as analytical grade. 85 wt. % H<sub>3</sub>PO<sub>4</sub> was bought from Solvay Chemicals. *N*-methylpyrrolidone (NMP) was received from BASF SE.

#### 4.1.2 Epitaxial GaN Wafers

Standard c-plane oriented GaN epilayers were grown in commercially available MOCVD reactors. Planar sapphire wafers were used as growth substrates during epitaxy. Prior to GaN epitaxy, a thin AlN nucleation layer was deposited on the sapphire substrates to achieve Ga-polar growth direction. 2 inch GaN substrate wafers were used with a TD density of  $2.0 \cdot 10^6$  cm<sup>-2</sup>.

#### 4.1.3 GaN Sample Processing

**Chip Processing** Sapphire wafers with epitaxial GaN layers were coated with an Au-Sn lot metal stack and solder bonded to planar silicon wafers. Subsequently, 20 nm Pt were deposited on the silicon back side to prevent silicon etching in hot KOH solution. By LLO, the sapphire substrate was removed to reveal the N-face of GaN. Afterwards, the prepared wafers were cut into  $1 \cdot 2$  cm rectangular pieces, which served as a sample material for etch experiments. The saw trench had a width of 40 µm. The effective error in sample area caused by the saw trench was not considered due to the minimal relative impact. Selected experiments were conducted with entire wafers. This was, however, not preferred due to material variation from wafer to wafer.

**Mechanical Polishing** If indicated, GaN was polished on a commercially available fully automated grinder/polisher. A commercially available slurry was used with pH 12.3. A mechanical component based on  $SiO_2$  was used. 3 or 8 cycles polishing corresponded to total polishing times of 48 s or 128 s, respectively. Depending on the respective GaN material, the appropriate polishing time was selected and will be indicated later on.

**BOE Pretreatment** In experiments without surface polishing, decomposition residues from LLO (i.e., elemental Ga and  $GaO_x$ ) were removed by immersion of the GaN samples in BOE solution for 5 min at RT. Afterwards, the GaN chips were rinsed in deionized water (DIW) and dried on air at 75 °C. All visible residues were removed (Figure 4.1, top right). Also, treatment of a polished and smooth GaN surface with BOE solution showed no BOE attack on GaN itself (Figure 4.1, bottom right).

#### 4.1 Materials



Figure 4.1: SEM images of a non-polished GaN surface after 1 min (top left), 2 min (top center) and 5 min (top right) immersion in BOE solution at RT. Ga and  $\text{GaO}_x$  residues vom LLO were effectively removed by 5 min etching in BOE. SEM images of polished GaN surface after 1 min (bottom left), 2 min (bottom center) and 5 min (bottom right) immersion in BOE solution at RT. GaN was not attacked by BOE, which was visible by means of the smooth surface after immersion for 5 min.

SiN<sub>x</sub> Grid Deposition To relocate a certain position on the GaN surface before and after etching, no photoresist could be used. The latter are generally unstable in aq. KOH solution at elevated temperature. Instead, 300 nm SiN<sub>x</sub> were deposited in a chemical vapor deposition (CVD) process from silane and nitrogen. NH<sub>3</sub> was thereby removed from the reactor to increase the SiN<sub>x</sub> stability against KOH. Before SiN<sub>x</sub> deposition, the GaN surface was cleaned with BOE treatment for 5 min. The SiN<sub>x</sub> layer was structured with a photo resist and BOE etching at RT for 30 min. In the last step, the photo resist was removed with acetone to provide a KOH stable grid (Figure 4.2).

Noble Metal Grid Deposition Epitaxial GaN wafers were immersed in 10 wt. % aq. HF solution for 10 min at RT to remove LLO damage. A photo resist pattern was applied with  $100 \cdot 100 \text{ µm}^2$  field size and 35 nm uncovered stripes in between. Further on, 100 nm Au or Pt were physical vapor deposited. The photo resist was removed by solvent lift off with NMP.

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Figure 4.2: SEM images of GaN surface section after application of a KOH-stable  $SiN_x$  grid by CVD and structuring with photoresist and BOE etching. With the aid of the  $SiN_x$  grid, a certain position on the sample could be relocated during SEM analysis after etching. Thereby, consequential surface analysis over the etch time was enabled.

# 4.2 Etch Setup

Standard etching of GaN sample pieces was performed in 50 mL polypropylene centrifugal vials containing 20 mL aq. KOH solution under magnetic stirring. After 10 min preheating in an ethylene glycol heating bath, the KOH solution temperature was controlled with a Basetech IRT-350 laser thermometer to prevent cooling of the solution caused by a standard thermometer dipped into solution. The temperature could be maintained over the etch process with an uncertainty of  $\pm 1.5$  °C. The laser thermometer showed perfect agreement with a regular capillary thermometer. One  $1 \cdot 2 \text{ cm}^2$  GaN sample was immersed into 20 mL KOH solution for a specific etch time. After etching, GaN samples used for further characterization were rinsed in DIW and dried on air at 75 °C. Spray acid tool (SAT) etching of 6 inch GaN wafers was conducted on a commercially available etch tool. The first wafer of the batch was shielded by a KOH resistent dummy wafer to provide identical KOH solution contact for all GaN wafers.

# 4.3 ICP-OES Analysis of Etch Rate

For GaN ER determination, ICP-OES was conducted on commercially available Thermo Fisher iCAP devices. Plasma conditions were 1150 W power, 1.5 L min<sup>-1</sup> support gas stream, 0.5 L min<sup>-1</sup> spray gas stream and 12 L min<sup>-1</sup> cooling gas stream.

#### 4.3.1 Sample Preparation

From the initial 20 mL KOH solution, in which etching was performed, 250 µL samples were drawn after varying time increments. Each of the drawn samples was added to a prepared mixture of 9.25 mL DIW and 500 µL p.a. grade 36 wt. % HCl. This dilution was directly measured after foregoing calibration of the ICP-OES method. Acidification of the samples with HCl was applied to increase measurement precision by maximized solubility and minimized analyte adhesion to the tube inside walls.

#### 4.3.2 Development of Measurement Method

Whereas the silicon backside of the GaN sample pieces was protected by a deposited Pt layer, the silicon side-walls were still exposed to etching. Silicon was thus included in the ICP-OES method. By comparison of Si and Ga concentrations, measurement errors could be distinguished from sample taking errors. The element-specific wavelengths 417.206 nm and 288.158 nm for Ga and Si were evaluated, respectively. To achieve perfect matrix adaption, both low and high standard solutions contained identical KOH and HCl concentrations as the diluted sample. The low standard solution was prepared by adding 5 mL p.a. grade 36 wt. % HCl and 2.5 mL 30 wt. % KOH solution (unless otherwise indicated) to DIW to achieve a total volume of 100 mL. To this solution, varying concentrations between  $1 \text{ mg L}^{-1}$  and  $5 \text{ mg L}^{-1}$  Ga and Si were added to prepare the high standard solution. The concentrations of Ga and Si were adapted to the expected element concentrations in the samples. By matching the analyte concentrations in high standard and sample solution, maximum precision was reached. Varying KOH concentrations in the standard solutions were setup for kinetics determination of experiments with varying KOH concentrations. Thereby, perfect matrix adaption was reached in all ICP-OES measurements.

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#### 4.3.3 Calculation of Average Etch Depth

From the measured concentration of dissolved Ga in KOH solution, the average etch depth z (GaN) [nm] was calculated. The determination via ICP-OES had significant advantages over other reported ER determination techniques, which are height profiling and weighing before and after etching. Both these methods have the disadvantage that the samples have to be cleaned and dried between etching and measurement. Thus, surface oxidation on air leads to a quicker dissolution of the formed gallium-oxygen species during a subsequent etch step. Consecutive determination of etch depth dependent reaction kinetics is thus distorted by systematic overestimation of the Ga concentration. Furthermore, height profiling is imprecise due to the formation of pyramids with a height up to to 4 µm. At an ER of ~ 150 nm min<sup>-1</sup>, the exact position, in which height measurement is conducted, causes an error of up to 2600 %. For ICP-OES analysis of the average etch depth, however, the etch process did not have to be interrupted allowing for subsequent sample taking with fine intervals. Thus, this novel method enabled time- and depth-dependent ER determination and a resolution of the entire epitaxial stack design.

First, the mass of dissolved GaN in solution was calculated from the Ga concentration measured by ICP-OES according to

$$m(GaN) = \beta(Ga) \cdot 40 \cdot V(\text{KOH solution}) \cdot \frac{M(GaN)}{M(Ga)} + m_d(GaN) \quad . \quad (4.1)$$

Hereby,  $\beta$  (Ga) [mg L<sup>-1</sup>] was directly received from ICP-OES measurement. The factor 40 represents the dilution of 250 µL Ga-containing KOH solution in a total volume of 10 mL, which served as the solution measured by ICP-OES. The Ga concentration inside the etch solution was then multiplied by its volume (e.g., 20 mL in case of the first taken sample). The dissolved GaN mass was calculated from the Ga mass by consideration of the respective molar masses M (Ga) and M (GaN).  $m_d$  (GaN) refers to a correction regarding the particular GaN mass which had been removed from the solution during preliminary sample taking. It was calculated by

$$m_d^{t_2}(\text{GaN}) = m_d^{t_1}(\text{GaN}) + \beta^{t_1}(\text{Ga}) \cdot 2.5 \cdot 10^{-4} L \cdot \frac{M(\text{GaN})}{M(\text{Ga})}$$
 (4.2)

In this equation,  $t_1$  refers to the sample time directly before  $t_2$ . The value of  $m_d^{t_2}$  (GaN)

was then calculated by addition of  $m_d^{t_1}$  (GaN) to the GaN mass removed during the last sample taking at  $t_1$ . The respective Ga concentration  $\beta^{t_1}$  (Ga) [mg L<sup>-1</sup>] was therefore multiplied with the sample volume of 250 µL and transferred into the corresponding GaN mass.  $m_d$  (GaN) only contributed to a small correction, but was included regardless. The literature density of GaN  $\rho$  (GaN) = 6.10 g cm<sup>-3</sup> was used to calculate the average GaN etch depth z (GaN) [nm] [108].

$$z (\text{GaN}) = \frac{m (\text{GaN}) \cdot 10^{-3} \frac{\text{g}}{\text{mg}}}{6.10 \,\text{g} \,\text{cm}^{-3} \cdot 2 \, cm^2} \cdot 10^7 \frac{\text{nm}}{\text{cm}}$$
(4.3)

z (GaN) [nm] was plotted against the etch time t to investigate time- and depthdependent information on the etch kinetics. Based on that, the ER [nm min<sup>-1</sup>] was determined by fitting a first order term to the linear etch kinetics section.

#### 4.3.4 Precision and Reproducibility Evaluation

Errors of z (GaN) were determined by the standard deviation of the mean (SDM) of at least 3 independent single experiments, which were conducted under identical experimental conditions. The number of single experiments leading to a certain error will be given as n in the following chapters. The SDM was calculated as

$$SDM = \sqrt{\frac{\sum_{i=1}^{n} (z_i(\text{GaN}) - \overline{z}(\text{GaN}))^2}{n}}$$
 (4.4)

Hereby,  $\overline{z}$  (GaN) refers to the average value of at least 3 individual experiments, n is indicated under each plot. Errors in the ER were determined from individual etch experiments as well. Again, the number of single experiments will be indicated as n in the following chapters.

Measurement precision was evaluated by dissolution of a known amount of elemental Ga, which was determined by weighing before, in aqua regia for 3 d at RT. The resulting solution was diluted to match the Ga concentration with the ICP-OES high standard solution. Also, KOH and HCl were added to match both matrices. The calculated Ga concentration based on the actual mass of dissolved Ga was  $0.909 \text{ mg } L^{-1}$ . ICP-OES analysis yielded  $0.902 \text{ mg } L^{-1}$  Ga and thus a mismatch of 0.8 %.

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The reproducibility of the ICP-OES method was evaluated by etching of four nominally identical GaN chips for 1 h at RT [109]. The samples showed the initial LLO surface damage as no pretreatment was conducted. After etching, of each KOH solution three dilutions for ICP-OES measurement were prepared. The total number of 12 samples were analyzed by ICP-OES four times each (Figure 4.3). Fourfold analysis of an identical KOH dilution yielded z (GaN) = 249 ± 3 nm average GaN removal and thus a relative error of 1% (mean ± SDM, n = 4). Analysis of three different solutions drawn from an identical KOH sample led to z (GaN) =  $250 \pm 3$  nm also resulting in a relative error of 1% (mean ± SDM, n = 3). Finally, analysis of four different GaN chips from an identical epitaxial wafer etched under identical conditions gave z (GaN) =  $246 \pm 8$  nm equaling a 3% relative error (mean ± SDM, n = 4). As a consequence, the analysis error was significantly lower than the material variation error. Even with GaN chips taken from an identical epitaxy wafer, which was the lowest reachable material variation, the developed ICP-OES method had sufficient reproducibility to monitor the etch kinetics with high precision.

Regarding the ICP-OES measurement itself, the spectroscope was recalibrated at the latest after 10 measurements by measurement of low and high standard solutions to circumvent drifting.

In conclusion, a novel method was developed to determine the GaN etch kinetics with unprecedented precision under application of ICP-OES. Significant effort was put into the optimization and characterization of measurement error. Compared to the lowest possible material variation of 3 % relative error, the ICP-OES method reached 1 % relative error. Measurement precision analysis yielded a mismatch of only 0.8 % relatively to the known weighed amount of GaN inside the analyzed solution. Both reproducibility and precision were more than sufficient to resolve the effect of all material changes on the ER.



Figure 4.3: Evaluation of ICP-OES measurement reproducibility based on fourfold measurement of three dilutions drawn from four KOH solutions of individually etched GaN samples [109]. The measurement error caused by ICP-OES was significantly lower than the error caused by material variation between GaN samples 1-4. The respective relative SDM values were 1% (ICP-OES measurement), 3% (KOH sample taking) and 3% (GaN sample variation). The developed ICP-OES method had sufficient precision to monitor small changes in the etch kinetics due to material- or process-variation.

## 4.4 WLI Analysis of Surface Roughness

White light interferometry (WLI) was measured on a commercially available interferometer. As measurement parameters, a 50 × lens was used with 2 × multiplication, 5 µm back scan and 25 µm z-scan length. The resulting sample area had  $60 \cdot 47.5 \,\mu\text{m}^2$ dimensions. Filtered light with a wavelength of 567 nm was used. WLI offered a fast method for surface roughness analysis, which is next to material removal the critical output of etch processing. Due to the optical measurement principle, the resolution is limited to  $\sim \frac{1}{4} \lambda$ , which corresponds to  $\sim 142 \,\text{nm}$ . Small pyramids could therefore not be resolved. However, also the emitted LED light underlies this limitation so that optical roughness measurement suited the LED application very well. The roughness value evaluated during WLI analysis was  $S_q$ , which represents the 2D root mean square (RMS) roughness. It was determined directly in the analysis software Bruker Vision64.

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$$S_q = \sqrt{\frac{1}{A} \int_{x_0}^{x_1} \int_{y_0}^{y_1} z^2(x, y) dx dy}$$
(4.5)

Hereby,  $x_0$ ,  $x_1$ ,  $y_0$  and  $y_1$  are the dimensions of the measured sample field, whereas A refers to the total measured area  $(x_1-x_0) \cdot (y_1-y_0)$ . The two-dimensional roughness  $S_q$  was preferred over the one-dimensional parameter  $R_q$  to investigate more data points and thus achieve an increased statistical significance as well as a higher reproducibility.

#### 4.4.1 Comparison between AFM and WLI

On a single GaN sample piece, WLI was compared to AFM. AFM, which was considered as the reference method, was performed on a commercially available Veeco/Bruker microscope. A Scanasyst-Air tip with 2 nm diameter was used. All measurements were recorded in peak force tapping mode with 2 kHz frequency. For comparison between WLI and AFM, a GaN sample was etched in 30 wt. % aq. KOH solution at 80 °C for 6 min. AFM images were taken in 4 positions on the sample surface with  $20 \cdot 20 \,\mu\text{m}^2$  scan dimensions (Figure 4.4). The  $S_q$  roughness was determined by AFM to be  $528 \pm 22$  nm (mean  $\pm$  SDM, n = 4, Table A.1). Compared to that, WLI analysis gave  $925 \pm 204$  nm  $S_q$  (mean  $\pm$  SDM, n = 5, Table A.2). The SDM calculated from WLI data was significantly higher with 22% compared to 4% in case of AFM. As the sample fields of AFM and WLI were not identical, however, local differences in surface morphology played an important role (e.g., wafer bow, surface damage prior to etching). The offset in the mean value and SDM was caused by the difference in power spectrum density. Due to the higher resolution of AFM and the smaller sample field, the range in surface feature size differed between AFM and WLI. On the one hand, WLI had a larger sample size and thus a higher statistic significance. Also, macroscopic effects like wafer bow increased the determined  $S_q$ . On the other hand, the higher resolution during AFM measurement included microscopic pyramids, which were too small for WLI measurement, into the calculation. Direct compatibility between the roughness parameters of WLI and AFM analysis was thus not given. The  $S_q$  values could only be compared between samples, provided that the analysis technique was unchanged.



**Figure 4.4:** AFM images of four individual positions on an identical GaN sample after etching in 30 wt. % aq. KOH solution for 6 min at 80 °C. In the order top left, right and bottom left, right, the determined  $S_q$  values were 548 nm, 532 nm, 552 nm and 527 nm.

#### 4.4.2 WIW Non-uniformity Determination on 6 Inch Wafer

WLI analysis was used to determine the <u>within</u> wafer etch non-uniformity (WIW) on a 6 inch wafer. For that, a 51-point recipe for automated measurement was created (Figure 4.5). The wafer was measured in x- and y-direction in small steps for detection of radius dependent  $S_q$  differences. Also, 12 additional points were included in between the x- and y-axes to detect further angle-dependent non-uniformity.

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Figure 4.5: Wafer map with WLI coordinates for determination of  $\overline{S_q}$  over 51 points. The wafer edge exclusion was 4 mm. WLI analysis was conducted to determine the etch uniformity across an entire 6 inch wafer. The radius-dependent uniformity was measured with high resolution along the x-and y-axes. 12 additional points were included to further detect angular uniformity differences.

WIW was calculated according to

$$WIW = \frac{SDM (n = 51)}{\overline{S_q}} \quad . \tag{4.6}$$

Hereby, SDM is the standard deviation of the mean of  $S_q$  values determined at all 51 coordinates.  $\overline{S_q}$  represents the average  $S_q$  value of all 51 single measurements. The industry standard formula for  $WIW_{max-min}$  determination comprising the maximum and minimum values max and min was not chosen to decrease the impact of measurement outliers, that are regularly observed during WLI analysis.

$$WIW_{max-min} = \frac{max - min}{2 \cdot \overline{S_q}} \tag{4.7}$$

The reproducibility of the WLI method was evaluated with the help of a 6 inch GaN wafer roughened by immersion in 30 wt. % aq. KOH solution for 7 min at 80 °C. Etching led to a weight loss of 170.4 mg and a calculated average material removal of 1574 nm. The wafer was measured three times in a row showing good reproducibility of WIW

(Table 4.1). The mean roughness  $\overline{S}_q$  as well as the SDM (n = 51) were almost identical in all cases. WIW had a value of ~7%. Compared to that,  $WIW_{max-min}$  had significantly higher values between 16% and 18%. The higher  $WIW_{max-min}$  did not represent the wafer surface. It was a measurement error, which stemmed from the surface feature size at the edge of resolution of optical analysis. The optimum surface roughness was set to be > 450 nm to achieve surface facets large enough for light transmission. The optimum WIW was 0% representing a perfectly homogeneous surface without local inhomogeneity in roughness.

In summary, a WLI analysis method was developed to characterize the surface roughness homogeneity on an entire 6 inch wafer. Thereby, the 2D surface roughness  $\overline{S}_q$  was determined in 51 positions on the wafer. The coordinates were separated in x- and y-direction with high measurement density. Additional coordinates were inserted off axes to detect further non-symmetrical inhomogeneity. The WLI method based on optical measurement was highly suitable for characterization of the optical light emission properties.

Measurement entry	$\overline{S_q}$ / nm	SDM $S_q$ / nm	WIW	$WIW_{max-min}$
1	597	40	7%	18%
2	580	40	7%	17%
3	589	36	6%	16%

**Table 4.1:** WLI determined surface roughness on a single 6 inch GaN wafer after roughening in 30 wt. % aq. KOH solution at 80 °C for 7 min. Both the average  $\overline{S_q}$  over all 51 points and the calculated uniformity parameters SDM  $S_q$ , WIW and  $WIW_{max-min}$  were reproducible.

# 4.5 Further Experimental Methods

**Crystal Quality** PLM images were recorded on a commercially available Olympus microscope combined with an Olympus UV light source. For excitation of the MQW, light with a wavelength of 408 nm was used. XRD was measured on a Bruker/Jordan Valley tool. CLM was measured on a commercially available Attolight tool.

**Surface Properties** SEM images were recorded on a commercially available Zeiss microscope with an acceleration voltage of 2 keV. Unless otherwise indicated, SE2 detection was used. Energy dispersive x-ray spectroscopy (EDX) was conducted on a commercially available Zeiss SEM tool in combination with an Ametek EDX system. An acceleration voltage of 5 keV was applied for excitation. XPS as well as Auger electron spectroscopy (AES) were performed on a commercially available Thermo Fisher tool. Irradiation energy was set to 10 keV at a 90° angle relatively to the sample surface. The dwell time was kept at 100 ms with 1 eV energy steps. Focused ion beam (FIB) cutting was performed on a commercially available FEI tool under use of a Ga ion source.

**NH<sub>3</sub> Detection** Two approaches were conducted to investigate NH<sub>3</sub> formation during GaN etching. First, a wet Roth pH-Fix indicator stick was placed above 20 mL 30 wt. % aq. KOH solution in a closed 50 mL polypropylene vial. Both with and without GaN in KOH solution, the sample was heated slowly to 50 °C under stirring. During heating, the changed pH was read from the test stripe. Also, NH<sub>3</sub> was detected by the Berthelot reaction [110]. 20 mL 30 wt. % aq. KOH solution were heated to 80 °C. Then, a GaN sample was added followed by 100 µL NaOCl solution (14% available chlorine). A spatula tip of added thymol formed a liquid organic phase in form of a droplet on top of the stirred hot KOH solution. The droplet had a slight brownish discoloration. In case of NH<sub>3</sub> formation, a blue color of the droplet was observed as well as a yellow color of the aq. phase. Both detection methods for NH<sub>3</sub> formation were conducted with several control experiments.

**Electron Beam Irradiation** Electron beam irradiation was realized by a Horiba Clue RPM and CL Link system built into a commercially available Zeiss SEM.

# 5 Influence of Epitaxial Growth Conditions on Etch Rate

Epitaxial growth conditions have a major impact on the number and propagation direction of TDs, which has been reported in literature many times. Their effect on the wet-chemical ER was investigated in a quantitative manner. For the reduction of TD density, different sequences of GaN layers with a combined thickness of several µm are commonly grown and summarized as the "GaN buffer layer". By purposeful control of the growth conditions, TDs, which tend to follow the growth direction, can be bent into lateral direction and eventually be terminated. The GaN buffer layer is revealed by LLO during chip processing. Its time- and depth-dependent etch kinetics were investigated and are discussed in the following experiments. For that, a novel high precision analysis method based on ICP-OES analysis was applied.

# 5.1 Epitaxial Buffer Layer Stack

For epitaxial growth, sapphire substrates with a thin AlN nucleation layer were used. Subsequently, unintentionally doped GaN (u-GaN) was deposited in 2D growth mode. This first GaN layer is referred to as 2D GaN. Sample **A**, which will serve as a reference in the following discussion, was designed with a 2D GaN thickness of 300 nm. Subsequently, a subatomic SiN<sub>x</sub> layer with a surface coverage of ~ 70 % was deposited. On top of the latter, the growth mode changed to 3D due to the SiN<sub>x</sub> layer. Thereby, a linear decrease of the molar NH<sub>3</sub>:(CH<sub>3</sub>)<sub>3</sub>Ga ratio from 3.0 to 1.0 relatively to the 2D growth conditions was applied. This second GaN layer is referred to as 3D GaN. Sample **A** featured a 3D GaN thickness of 1400 nm. Further on, a second 2D GaN layer (2D-2 GaN) was deposited. Etching of the latter was not considered anymore. For PLM analysis, a rudimentary GaN/In<sub>x</sub>Ga<sub>1-x</sub>N MQW was grown on top of the structure. Analysis of the MQW emission was used to only observe TDs, which penetrated the entire epitaxial layer. Also the MQW was not part of the etch experiments.

A schematic of the epitaxial layer stack as well as the flip-chip processed and etched sample are shown in Figure 5.1, left and center. By LLO, the sapphire substrate was removed. The first GaN layer subjected to KOH etching was the 2D GaN layer. The TD density of **A** was determined by a combination of XRD and PLM analysis ( $\lambda = 450$  nm, Figure 5.1, right). The FWHM peak width of the (102) reflex was 170 arcsec. PLM resulted in an absolute TD density of  $1.3 \cdot 10^8$  cm<sup>-2</sup>. This value refers to the dislocations reaching all the way through the GaN buffer layers and into the MQW. The XRD value can be seen as integral over the entire epitaxial layer stack, as the method functions independently from MQW emission.



Figure 5.1: Schematic epitaxial layer stack **A** before chip processing (left). The schematic is pictured upside-down. Directly on the sapphire substrate, a thin AlN nucleation layer was grown followed by 300 nm GaN deposited under 2D conditions. By insertion of a single atom layer SiN<sub>x</sub> with a surface coverage of ~70%, 3D growth occurred afterwards. By TD bending, the TD density of 3D GaN was reduced from >4 \cdot 10<sup>8</sup> cm<sup>2</sup> (2D GaN) to  $1.3 \cdot 10^8$  cm<sup>2</sup>. Schematic cross section of chip flow processed sample **A** after LLO (center). PLM ( $\lambda = 450$  nm) image for TD density analysis (right). Individual TDs are visible as dark spots in the otherwise blue emitting GaN material.
# 5.2 General Etch Kinetics

The etch kinetics of  $\mathbf{A}$  were analyzed by ICP-OES after etching in 30 wt. % aq. KOH at 80 °C for 5 min (Figure 5.2). Hereby, z (GaN) [nm] refers to the average material removal reached by the etch progress. An etch depth of 0 nm represents the GaN surface initially revealed by LLO. The  $SiN_x$  layer, which corresponds to the transition from 2D GaN to 3D GaN, is marked by the red line at z(GaN) = 270 nm. The  $30 \,\mathrm{nm}$  difference between theoretical ( $300 \,\mathrm{nm}$ ) and actual ( $270 \,\mathrm{nm}$ ) depth stems from GaN decomposition caused by LLO processing. The initial ER between 0 and 200 nm material removal was high with a value of  $> 400 \text{ nm min}^{-1}$  due to the LLO surface damage. This led to undefined crystal facets facing towards the etch solution. The higher relative ER of other crystal facets than the developing pyramid side planes caused a higher etch removal until pyramid termination of the entire surface. The etch kinetics at 80 °C showed a plateau formation in the region of the  $SiN_x$  layer. From 45 s to 90 s, only very little average material removal was reached. After 2 min, a constant ER set in with a value of  $338 \pm 30$  nm min<sup>-1</sup> (mean  $\pm$  SDM, n = 3). The constant ER corresponded well to the previously reported linear etch progress, provided that the material composition was unchanged over the entire etch process [81]. To investigate the plateau formation, the experiment was repeated at 70 °C solution temperature. Again, after  $\sim 200 \,\mathrm{nm} \, z \,(\mathrm{GaN})$ , plateau formation occurred. The lower temperature led to a significantly increased plateau selectivity. Whereas the initial ER between 0s and 30 s etch time was only slightly lower at 70 °C, crossing of the plateau took 4 min instead of  $1.5 \min (80 \,^{\circ}\text{C})$ .

In conclusion, the individual ER of each epitaxial layer could be determined by ICP-OES with high precision. The highest ER was found in the 2D GaN layer. Thereafter, plateau formation occurred at the  $SiN_x$  interface. Plateau formation was elongated by the temperature decrease from 80 °C to 70 °C. Linear etching set in once the 3D GaN layer was reached.

#### 5 Influence of Epitaxial Growth Conditions on Etch Rate



Figure 5.2: Schematic epitaxial layer stack of A overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at 70 °C and 80 °C. The data is presented as mean  $\pm$  SDM, n = 3. After 270 nm average material removal, plateau formation was observed. Thereafter, a constant ER set in. Whereas the plateau was crossed after a time span of 4 min in case of 80 °C, crossing took 4 min at a lower temperature of 70 °C. This showed the temperature-dependency of plateau selectivity.

# 5.3 Development of Surface Morphology with Increasing Etch Removal

To investigate the plateau formation observed in the etch kinetics, the surface of **A** was analyzed by SEM after consecutive etch times between 0 min and 10 min (Figure 5.3, Figure 5.4). The identical surface section was relocated by deposition of a KOH stable SiN<sub>x</sub> grid, which was described in chapter 4. Before BOE pretreatment and KOH etching, Ga and GaO<sub>x</sub> decomposition products were visible on the surface (Figure 5.3, top left). These residues were removed during BOE pretreatment, so that the surface prior to KOH etching only showed LLO surface roughness in form of ridges (Figure 5.3, top right). This surface morphology is characteristic for LLO separated GaN-sapphire interfaces. It is a consequence of thermal decomposition by laser irradiation and mechanical force caused by expansion of the developing nitrogen gas. After 1 min etching, a flat surface was found, on top of which single small 2D GaN pyramids had remained (Figure 5.3, middle left). The flat surface represented the plateau observed in the etch kinetics and was located at the SiN<sub>x</sub> interface between 2D and 3D GaN. The small pyramids remaining on the surface stemmed from the quickly etched 2D GaN layer, which at this point had been almost entirely dissolved.



Figure 5.3: SEM image of GaN surface after LLO showing liquid Ga in form of bright droplets and solid  $GaO_x$  decomposition products in form of dark discolorations (top left). SEM images of identical surface section (GaN epitaxial layer A) after 0-4 min etching in 30 wt. % aq. KOH solution at 80 °C. Plateau formation after 1 min etching as well as the steady increase in average pyramid size during subsequent etching are visible. Due to etching of the KOH-stable  $SiN_x$  used for relocation of the exact same surface section, the necessary immersion in BOE solution also removed Ga and  $GaO_x$  residues. This resulted in the clean surface visible in the top right image. The scale bar included in the bottom right corner refers to all images except top left.



Figure 5.4: SEM images of identical surface section A after 5-10 min etching in 30 wt. % aq. KOH solution at 80 °C. The steady increase in average pyramid size over etch time is visible. The scale bar included in the bottom right corner refers to all images.

After 2 min etching, the entire GaN surface showed formation of small pyramids in form of a nano-roughness (Figure 5.3, middle right). These initial pyramids evolved larger up to a combined etch time of 10 min. From 2 min to 10 min, the surface coverage with pyramids was > 90 %. This explained well the constant ER observed in the etch kinetics. In general, the total area of a pyramidal surface morphology is independent from pyramid size as long as the base plane area, the side plane angles and the pyramid coverage remain unchanged (Figure 5.5). In this schematic, it is clearly visible that the red left pyramid facet of the large pyramid can be set together by combination of all left red facets of small pyramids. Thereby, the angle of the side facets as well as the combined pyramid base length remains identical regardless of pyramid size. Transferred to the actual etch sequence, both the area and the kind of crystal facets subjected to the KOH solution were identical from 2 min to 10 min. As a consequence, also the ER from 2-10 min was constant.



Figure 5.5: Schematic model of pyramid surface. As long as the pyramid base plane area and the side plane angle are identical, the height and number of individual pyramids does not alter the total surface area subjected to KOH solution. The surface area of a larger pyramid, which evolves after a prolonged etch time, is identical to the combined surface of small pyramids present at an earlier stage of the etch process.

The crystal facets forming the pyramid side planes have been discussed controversially in literature [63, 81, 111]. AFM analysis of the surface angles was therefore conducted to determine the precise angle of the side planes relatively to the  $(000\overline{1})$  base plane. This resulted in an angle of  $61.5 \pm 0.6^{\circ}$  (Figure A.1, mean  $\pm$  SDM, n = 3). The determined angle conforms well with the theoretical angle of  $62.1^{\circ}$ , which  $\{10\overline{11}\}$  facets form with the lateral  $(000\overline{1})$  base plane.

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With a constant  $\{10\overline{11}\}$  coverage of the surface, one would expect that the sizes of all pyramids should remain unchanged because all pyramid side facets are etched at the same ER (Figure 5.6, left). Therefore, the number and position of pyramid tips should actually remain identical from that point on. However, the average pyramid size was found to steadily increase (Figure 5.6, right). Single pyramids coalesced to large ones, the tip of which was later on broken down into smaller pyramids again (Figure 5.7). *Etching thus occurred as a constant equilibrium of pyramid formation and erosion* [94]. The positions of pyramid tips remained identical during the course of seconds to at most 2 min. The underlying reason for the increase in average pyramid size and the observed instability of pyramid tips will be discussed in a later section of chapter 8.



Figure 5.6: Schematic model of the hypothetical development of the pyramidal surface morphology only considering the constant etch removal of all pyramid side facets (left). In this situation, the average pyramid size would remain unchanged. Schematic model of the actual increase in average pyramid size (right). During etching, GaN pyramids evolve larger constantly. At one point, a tip is eroded so that the large pyramid is broken down into smaller pyramids again. Pyramid tips were found to be stable over a time span of at most 2 min.



Figure 5.7: Excerpts of SEM images (Figure 5.3, Figure 5.4) showing the formation and dissolution of a large pyramid over the course of 5 min etching. The tip position of the largest pyramid stadium is indicated by the red dot. After formation of a large pyramid, the tip of the latter was eroded. Thereby, formation of multiple small pyramids was initiated again.

# 5.4 Plateau Formation at SiN<sub>x</sub> Interface

## 5.4.1 Resolution of Plateau Formation under SEM

To investigate the mechanism of plateau formation observed in the etch kinetics of  $\mathbf{A}$ , several samples  $\mathbf{A}$  were etched to reach ~275 nm material removal. In increasing order of etch depth, SEM analysis was conducted (Figure 5.8). The sample with the lowest material removal showed bright 2D GaN pyramids on top of a (000 $\overline{1}$ ) plateau (Figure 5.8, top left). After slightly more etch removal, the plateau covered almost the entire sample surface besides single remaining 2D GaN pyramids (Figure 5.8, top center). Most of the 2D GaN pyramids had been dissolved at that point. The plateau layer appeared as a hazy layer, which had been broken through in some positions. During subsequent further etching, larger areas of the layer had been initiated.

Across all of the sample surfaces, significant local variation in etch progress was observed. Whereas single 2D GaN pyramids were found in some positions, other areas of

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the plateau had already been broken through. This local etch inhomogeneity prevented an ICP-OES analysis of the material removal, which could only determine the *average* etch removal over the entire sample. The etch depth variation was larger across each sample than in between the samples.

The situation shown in Figure 5.8, bottom left, had only ~10% of the surface covered by the darker plateau layer. Once the plateau had been crossed completely, formation of a dense arrangement of  $\{10\overline{11}\}$  pyramid tips occurred across the entire GaN surface. The latter developed larger in size during subsequent etching (Figure 5.8, bottom center and right; compare to the total etch progress in Figure 5.3 and Figure 5.4).

In summary, the plateau formation observed in the etch kinetics was proven to occur at the  $SiN_x$  interface between 2D and 3D GaN. In increasing order of local material removal, the gradual crossing of the transition could be resolved by SEM analysis.



**Figure 5.8:** SEM images of GaN samples **A** after etching in 30 wt. % aq. KOH solution at 80 °C to reach ~ 275 nm material removal. From top left to right and subsequently bottom left to right the images are in ascending order of local material removal. 2D GaN pyramids, which appear bright in the top left image, were progressively etched. Thereafter, the whole surface was covered by the hazy  $SiN_x$  layer (top center), which had already been broken through in some positions (top right). The bottom left image shows the dark  $SiN_x$  layer only covering a small section of the surface. After complete removal of the  $SiN_x$  layer, 3D GaN etching occurred. This was indicated by the increasing average pyramid size. The scale bar refers to all images.

## 5.4.2 Variation of SiN<sub>x</sub> Position

To prove that the  $SiN_x$  transition was the root cause for plateau formation, another epitaxial layer stack **B** was designed. Hereby, the 2D GaN thickness between sapphire substrate and  $SiN_x$  layer was increased from 300 nm to 1000 nm. Besides that, sample processing was identical to **A**. The XRD FWHM peak width decreased from 170 arcsec to 161 arcsec, which showed a slight increase in crystal quality. This was caused by partial TD termination within the thicker GaN buffer layer stack. By ICP-OES, the etch kinetics of **B** were investigated during etching in 30 wt. % aq. KOH at 70 °C and 80 °C (Figure 5.9).

Also in case of **B**, the highest ER of was observed during the initial process and up to a material removal of ~600 nm. At 70 °C, the initial ER was >500 nm min<sup>-1</sup>. At 80 °C, an initial ER of >750 nm min<sup>-1</sup> was measured. Again, this was caused by the undefined crystal facets revealed by LLO surface damage. At 80 °C, a constant ER also set in after 900 nm average material removal, once a uniform pyramidal surface had been reached. This indicated that the plateau had been largely crossed. The total material removal of both samples **A** and **B** was identical after 5 min etching at 80 °C with values of  $1294 \pm 38$  nm and  $1337 \pm 91$  nm, respectively (mean  $\pm$  SDM, n = 3,



Figure 5.9: Schematic epitaxial layer stack of **B** overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at 70 °C and 80 °C. The data is presented as mean  $\pm$  SDM, n = 3. The increased 2D GaN layer thickness of **B** caused the plateau formation in the etch kinetics of **A** to disappear. Due to the larger 2D GaN pyramids after 1000 nm 2D GaN, the SiN<sub>x</sub> plateau was reached in a smaller surface area compared to **A**. Its influence on the etch kinetics was smeared out as a consequence.

compare Figure 5.2). At both investigated temperatures, the plateau formation was not as pronounced in case of B. In other words, the minimum ER was higher than in case of A at all times during the etch process.

The plateau formed during etching of **B** was found by SEM at ~700 nm average material removal, which was lower than the actual SiN<sub>x</sub> position (1000 nm). This discrepancy was caused by the larger average 2D GaN pyramid size in case of **B**, when the valleys in between the pyramids approached the SiN<sub>x</sub> layer. This is schematically shown in Figure 5.10. The SiN<sub>x</sub> layer is first reached in between the pyramids. At a maximum etch depth of 1000 nm, the 2D GaN pyramid size is larger after 1000 nm maximum etch depth than after 300 nm. This effect is a consequence of the steadily increasing pyramid size and surface amplitude. Thus, the combined pyramid volume V<sub>B</sub> is larger than V<sub>A</sub>. Considering that the initial ER decreased as soon as the pyramid valleys reached the SiN<sub>x</sub> layer, the average etch depth measured by ICP-OES was systematically decreased by V<sub>A</sub> or V<sub>B</sub>, respectively.

The difference between  $V_{\mathbf{A}}$  and  $V_{\mathbf{B}}$  could also explain the less pronounced plateau formation in the etch kinetics. The larger 2D GaN pyramids formed in case of **B** took longer to be etched entirely down to the  $SiN_x$  layer than the smaller pyramids in case of **A**. Thus, when large sections of the surface were still covered with 2D GaN



Figure 5.10: Schematic explanation of etch depth discrepancy between position of  $SiN_x$  layer and plateau in ICP-OES determined etch kinetics. The  $SiN_x$  layer is located at 300 nm (A, left) and 1000 nm (B, right), respectively. After 1000 nm maximum material removal, the remaining 2D GaN pyramids had a larger volume than after 300 nm. As a consequence, the determined average material removal was disproportionately lower in case of B.

pyramids in case of **B**, the intermediate  $SiN_x$  transition experienced longer etching. Therefore, it was broken through more quickly relatively to the total sample surface. As a consequence, the surface coverage with the more slowly etched  $SiN_x$  layer was lower in case of **B** at all times. The minimum average ER was higher at all times. *Effectively, the impact of the*  $SiN_x$  layer on the total etch kinetics was decreased by increasing the 2D GaN depth. SEM images of **A** after 246 nm and **B** after 739 nm average material removal were recorded at a 45° angle (Figure 5.11). The remaining 2D GaN pyramids in case of **B** were significantly larger compared to **A**. Simultaneously, the 3D GaN pyramids developing after  $SiN_x$  crossing were already larger than it was on the surface of **A**. The z-amplitude of surface features was larger at this point in case of **B**.



Figure 5.11: SEM images of representative samples A after an average etch depth of z (GaN) = 246 nm (left) and B after z (GaN) = 739 nm (right) recorded at an angle of 45°. A was prepared by etching in 30 wt. % aq. KOH at RT for 60 min. B was prepared by 2 min etching in 30 wt. % aq. KOH solution at 80 °C. The larger 2D GaN pyramids in case of B were proven by SEM analysis. The root cause for the discrepancy between theoretical position of the SiN<sub>x</sub> interface and the actual average material removal at its crossing was verified to be the combined volume of remaining 2D GaN pyramids.

## 5.4.3 Etch Kinetics of Bulk 2D GaN

To further investigate the plateau formation during etching of **B**, another epitaxial layer **C** was designed. The latter consisted out of a single  $3 \mu m$  GaN layer grown exclusively under 2D growth conditions. XRD analysis resulted in a FWHM peak width of 322 arcsec and thus a significantly higher TD density as it had been achieved

in samples **A** (170 arcsec) and **B** (161 arcsec). The reason for that was that no strategy for defect reduction had been applied besides the thin AlN nucleation layer. PLM analysis of a reference sample with a MQW yielded a TD density  $> 4 \cdot 10^8$  cm<sup>-2</sup>. The absolute value could not be determined due to clustering of TDs, which were not visible as individual contrasts in the PLM image. By ICP-OES, the etch kinetics were determined in 30 wt. % aq. KOH at 60 °C and 80 °C (Figure 5.12).

At 80 °C, the etch kinetics of **B** and **C** were identical up to an etch depth of 900 nm. From that point on, the ER of **B** was higher compared to **C**. The average material removal, that **B** reached after 5 min etching at 80 °C, was higher as well with a value of  $1337 \pm 91$  nm (mean  $\pm$  SDM, n = 3) compared to  $1145 \pm 72$  nm in case of **C** (mean  $\pm$  SDM, n = 4). Consequentially, the SiN<sub>x</sub> transition within **B** was visible under SEM (Figure 5.11, right), but had no measurable influence at all on the etch kinetics. Under the here applied growth and etch conditions, the 3D GaN layer had a higher ER compared to 2D GaN.



Figure 5.12: Schematic epitaxial layer C overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at 60 °C and 80 °C. The data is presented as mean  $\pm$  SDM, n = 8 (60 °C) and n = 4 (80 °C). Although the epitaxial GaN layer C was homogeneous, ER saturation occurred regardless. Also, an increased relative etch reproducibility at higher temperatures is indicated by the smaller error bars at 80 °C. Saturation occurred due to the initially undefined crystal facets on the surface. Once the undefined facets were transformed into regular pyramids, a lower and constant ER set in.

In fact, **C** showed saturation of the ER both at 60 °C ( $66 \pm 18 \text{ nm min}^{-1}$ ) and 80 °C ( $147 \pm 17 \text{ nm min}^{-1}$ ), although no SiN<sub>x</sub> interface was present. ER saturation had been previously attributed to plateau formation at the SiN<sub>x</sub> interface in case of **B**. However, the reason for that was found to be the development of surface angles during proceeding etch time. The initial surface after LLO is defective and has multiple and random crystal facets. Generally, pyramid formation occurs as a consequence of the greater stability of the pyramid side facets compared to other crystal planes accessible from the N-face of GaN. *Thus, the initial ER after LLO was higher until the surface was largely covered with* { $10\overline{11}$ } *pyramids.* A detailed discussion of the basis for anisotropic etching will be presented in chapter 8.

In conclusion, by removal of both  $SiN_x$  interface and 3D growth the plateau formation in the etch kinetics was effectively eliminated. The reason for the high *initial* ER in all experiments were undefined crystal facets on the surface, which had been caused by LLO damage. A constant ER was reached by the time at which the whole surface was covered with  $\{10\overline{11}\}$  pyramids.

## 5.4.4 Variation of SiN<sub>x</sub> Coverage

Another epitaxial layer stack was designed with a lower  $SiN_x$  coverage compared to **A** and **B**. The experiment aimed towards the separation of a low  $SiN_x$  ER itself or another possible influence of TD bending at the transition from 2D to 3D growth direction. D featured a SiN<sub>x</sub> coverage of ~20 % compared to ~70 % in case of A and **B**. Otherwise, the structure was identical to **A**. XRD analysis of the (102) reflex FWHM peak width yielded a value of 324 arcsec. The TD density was identical to C, which had yielded a FWHM of 322 arcsec. By PLM, the TD density was determined to be  $> 4 \cdot 10^8 \,\mathrm{cm}^{-2}$ . The TD bending into the lateral direction was fully circumvented by the lower  $SiN_x$  coverage. No effective 3D growth occurred. By ICP-OES, the etch kinetics were determined in 30 wt. % aq. KOH at  $80 \,^{\circ}\text{C}$  (Figure 5.13). In the plot, the layer above the  $SiN_x$  interface is still described as "3D", as the epitaxial growth conditions themselves were identical to  $\mathbf{A}$ . The etch kinetics of  $\mathbf{D}$  were almost identical to  $\mathbf{A}$ (Figure 5.2). Plateau formation occurred although 3D growth and dislocation bending had been eliminated. Crossing of the plateau took only  $\sim 1.0 \min(\mathbf{D})$  instead of 1.5 min (A). The lower  $SiN_x$  coverage indeed reduced the effective etch stop. This suggested that the  $SiN_x$  ER itself caused the etch stop.

Moreover, the ER of 3D GaN after crossing of the  $SiN_x$  layer was identical to **A**. This was the first experiment during the course of this work, which showed that TD density had no measurable influence on the average ER. As previously discussed, the TD density of **D** was ~4 times higher than the TD of **A**. Both plateau formation and the resulting ER were therefore independent from TD density.



Figure 5.13: Schematic epitaxial layer **D** overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at  $80 \degree$ C. The data is presented as mean  $\pm$  SDM, n = 3. Although 3D growth was effectively circumvented by a lower SiN<sub>x</sub> coverage, plateau formation occurred regardless. However, crossing of the plateau took less etch time than in case of **A**. Besides the altered SiN<sub>x</sub> interface, the growth conditions of the subsequent GaN were identical to the foregoing samples. Due to that, the layer is referred to as 3D GaN also in case of sample **D**.

## 5.4.5 Al<sub>0.11</sub>Ga<sub>0.89</sub>N Overgrowth of SiN<sub>x</sub> Layer

Although 3D growth was effectively circumvented in sample **D**, the 3D growth conditions during epitaxy in terms of V:III ratio were still different from the initial 2D GaN growth. Especially at a low V:III ratio, carbon implantation into the epitaxial layer occurs due to the precursor  $(CH_3)_3$ Ga. To eliminate the influence of growth conditions, epitaxial stack **E** was designed on the basis of bulk 2D GaN **C**. After 300 nm 2D GaN, a SiN<sub>x</sub> layer was grown with ~70 % surface coverage, as it had been in case of **A**. Subsequently, 30 nm Al<sub>0.11</sub>Ga<sub>0.89</sub>N were deposited. Thereafter, 2.7 µm GaN were grown under the initial 2D growth conditions. The total thickness of the epitaxial layer was thus similar to **C**.  $Al_{0.11}Ga_{0.89}N$  overgrowth of the  $SiN_x$  layer occurs unselectively both on  $SiN_x$  and uncovered GaN. GaN growth on top of  $Al_{0.11}Ga_{0.89}N$  therefore continues in 2D growth direction in the same way as it would function without a  $SiN_x/Al_{0.11}Ga_{0.89}N$  interlayer (compare to **C**). Lateral growth combined with dislocation bending was thus fully circumvented. At the same time, a regular  $SiN_x$  was included. XRD analysis of **E** resulted in 297 arcsec FWHM peak width of the (102) reflex. The crystal quality was in the range of **C** (322 arcsec), as it had been aimed for. By ICP-OES, the etch kinetics were determined during etching in 30 wt. % aq. KOH at 80 °C Figure (5.14). For comparison, the etch kinetics of **C** are also included in the plot, although the schematic layer stack only refers to **E**.



Figure 5.14: Schematic epitaxial layer stack  $\mathbf{E}$  overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at 80 °C. The data is presented as mean  $\pm$  SDM, n=4. For comparison, the etch kinetics of  $\mathbf{C}$  are also included in the plot in light grey, although the schematic layer stack does only refer to  $\mathbf{E}$ . By comparison between  $\mathbf{C}$  and  $\mathbf{E}$ , plateau formation in the latter case is clearly visible. The ER after crossing of the SiN<sub>x</sub>/Al<sub>0.11</sub>Ga<sub>0.89</sub>N interlayer ( $\mathbf{E}$ ) was identical to  $\mathbf{C}$ . Also the etch reproducibility was not altered.

Plateau formation was observed between 0.5 min and 1.0 min etch time. In this region, the lowest etch progress was achieved, especially compared to the etch kinetics of **C** (Figure 5.12). Whereas **C** had a total material removal of  $375 \pm 55$  nm after 0.5 min, the same etch time yielded a material removal of  $197 \pm 4$  nm in case of **E** (mean  $\pm$  SDM, n = 4). This discrepancy clearly showed the formed plateau. Also, the final material removal of **C** with a value of  $1145 \pm 72$  nm after 5 min etching was significantly higher than in case of **E** with a value of only  $761 \pm 57$  nm (mean  $\pm$  SDM, n = 4).

After the plateau formation, the ER of **E** reached a constant value of  $136 \pm 18 \text{ nm min}^{-1}$ immediately (mean  $\pm$  SDM, n = 4). In case of **C**, the initial higher ER saturated after 650 nm at a value of  $147 \pm 17 \text{ nm min}^{-1}$  (mean  $\pm$  SDM, n = 4). Therefore, the ERs of both epitaxial layers **C** and **E** were quasi identical regardless of the etch stop layer. The plateau created by the SiN<sub>x</sub>/Al<sub>0.11</sub>Ga<sub>0.89</sub>N interlayer had no influence on the ER of the underlying GaN, provided that the GaN growth conditions remained identical.

In conclusion, the  $SiN_x$  layer itself caused the etch stop. The plateau selectivity could be decreased by reducing the  $SiN_x$  coverage from ~ 70 % to ~ 20 %. Also, plateau formation still occurred when the GaN material grown below and above the  $SiN_x/Al_{0.11}Ga_{0.89}N$  interlayer was identical. Insertion of a  $SiN_x/Al_{0.11}Ga_{0.89}N$  interlayer only reduced the etch depth necessary for reaching a constant ER from ~ 650 nm to ~ 300 nm.

# 5.4.6 Temperature-Dependency of Plateau Selectivity

For renewed comprehension of the epitaxial layer stack designs  $\mathbf{A}$ ,  $\mathbf{C}$  and  $\mathbf{E}$ , the color schemes in the following Figures 5.15 and 5.16 can be consulted. At 80 °C solution temperature, the SiN<sub>x</sub> plateau of  $\mathbf{A}$  had been crossed after a time span of 1.5 min. As soon as the solution temperature had been lowered to 70 °C, crossing took 4 min (Figure 5.2).

The selectivity of plateau formation was investigated by etching of **A** and **C** in 30 wt. % aq. KOH at RT (Figure 5.15). **A** remained at a material removal of  $226 \pm 15$  nm from 20-50 min etching (mean  $\pm$  SDM, n = 3). The plateau selectivity at RT was therefore very high. **C**, which was etched without a plateau due to the missing SiN<sub>x</sub> interface, showed etching with an increased initial ER that saturated at a value of  $13 \pm 4$  nm min<sup>-1</sup> after ~ 600 nm material removal (mean  $\pm$  SDM, n = 5).

The etch reproducibility of different samples  $\mathbf{C}$  was lower at RT compared to 80 °C. This indicated that local material-dependent influences on the ER had a higher impact at RT. The etch selectivity between GaN and  $SiN_x$  became lower with increasing temperature. To reduce the impact of inconsistent material, a high solution temperature should be therefore chosen.

Also, the etch kinetics of **E** were determined by ICP-OES during etching in 30 wt. % aq. KOH at RT for 50 min (Figure 5.16). The etch plateau at the  $SiN_x/Al_{0.11}Ga_{0.89}N$ 



Figure 5.15: Schematic epitaxial layer stacks of A (left) and C (right) overlaid with their respective ICP-OES determined etch kinetics in 30 wt. % aq. KOH at RT. The data is presented as mean  $\pm$  SDM, n = 3 (A) and n = 5 (C). At RT, the SiN<sub>x</sub> interface acted as an effective etch stop layer, which could not be crossed within an etch time of 50 min. Compared to that, C showed a steady etch progress also at RT.



Figure 5.16: Schematic epitaxial layer stack **E** overlaid with ICP-OES determined etch kinetics in 30 wt. % aq. KOH at 80 °C. The data is presented as mean  $\pm$  SDM, n = 5. Also the SiN<sub>x</sub>/Al<sub>0.11</sub>Ga<sub>0.89</sub>N layer stack acted as an etch stop layer when etching was performed at RT.

interface of **E** was not crossed up to a total etch time of 50 min. The average material removal, which had been reached at that point, was  $259 \pm 7 \text{ nm} (\text{mean} \pm \text{SDM}, \text{n} = 5)$ . The insertion of an additional  $Al_{0.11}Ga_{0.89}N$  layer thus had no negative influence on the effective etch stop. For productive application, the insertion of a SiN<sub>x</sub> can thus act as an attractive approach for the design of an etch stop layer [112]. E.g., the entire

GaN buffer layer used for the reduction of TD density could be separated from the n-GaN layer by a  $SiN_x$  interface. If etching of the n-GaN layer was intended, further addition of an  $Al_{0.11}Ga_{0.89}N$  layer would supply identical etch properties of the n-GaN layer compared to its behavior without foregoing  $SiN_x/Al_{0.11}Ga_{0.89}N$ .

# 5.4.7 SiN<sub>x</sub> Insertion as an Effective Etch Stop Layer

Epitaxial layer stack  $\mathbf{F}$  was designed with two SiN<sub>x</sub> layers to investigate the above mentioned approach in terms of practical application. After the reference sequence of 300 nm 2D GaN, SiN<sub>x</sub> and 1400 nm 3D GaN (compare  $\mathbf{A}$ ), another stack of 600 nm 2D GaN, SiN<sub>x</sub> and 1400 nm 3D GaN was grown. Hereby, the TD density reaching the rudimentary MQW was determined to be  $1.1 \cdot 10^8 \text{ cm}^{-2}$  (Figure A.2, right). The FWHM peak width of the (102) reflex analyzed by XRD was 142 arcsec. The crystal quality reached by the increased buffer layer thickness as well as the second SiN<sub>x</sub> layer was the best of all conducted epitaxial runs, that had been discussed so far. First, etching was performed in 30 wt. % aq. KOH at 80 °C. The etch kinetics were monitored by ICP-OES (Figure 5.17).

The actual positions of the two  $\operatorname{SiN}_x$  layers were 300 nm and 2300 nm, respectively. Both were separated by 1400 nm 3D GaN and subsequently 600 nm 2D GaN. The latter was grown under the same conditions as the most substrate-near 2D GaN. At 80 °C, the plateau at the second  $\operatorname{SiN}_x$  could not be resolved. This corresponded well to the etch kinetics of **B**, where  $\operatorname{SiN}_x$  had no influence on the etch kinetics already at 1000 nm depth into the material.

However, SEM images of **F** showed small plateau sections in between of an otherwise pyramidal surface (Figure 5.18). By the large average pyramid size after 2300 nm average material removal, the valleys in between pyramids approached the second  $SiN_x$  layer only in a very small section of the sample surface. At 80 °C, the etch selectivity between  $SiN_x$  and GaN was too low to create an etch stop.

The previous knowledge was then applied to selectively stop the etch process at the second  $SiN_x$  interface. To accomplish this, the KOH temperature was decreased after crossing of the first  $SiN_x$  interface. In a first step, **F** was etched in 30 wt. % aq. KOH for 3 min at 70 °C to only cross the first  $SiN_x$  layer on the entire sample. This was confirmed by ICP-OES measurement of the Ga concentration in KOH solution, which showed an



Figure 5.17: Schematic epitaxial layer stack F overlaid with ICP-OES determined etch kinetics during etching in 30 wt. % aq. KOH at 80 °C. The data is presented as mean  $\pm$  SDM, n = 7. At 80 °C solution temperature, the second SiN<sub>x</sub> layer had no measurable influence on the etch kinetics. The reason for that was identical to the missing plateau in the etch kinetics of B. The percentage surface section in which the SiN<sub>x</sub> plateau was revealed was only very small after 2300 nm material removal.

average etch depth of  $265 \pm 11$  nm at that point (mean  $\pm$  SDM, n = 7). Subsequently, etching was performed at RT for 5 h. SEM images showed that the SiN<sub>x</sub> plateau had been approached, yet not crossed in large areas of the sample (Figure 5.19, left). Local differences in the ER, however, caused large remaining 2D GaN pyramids (Figure 5.19, center and right). These remaining pyramids decreased the actual average material removal after the combined process time to  $1425 \pm 116$  nm (mean  $\pm$  SDM, n = 3), which was measured by ICP-OES. This combined material removal was significantly lower than the theoretical SiN<sub>x</sub> depth of 2300 nm.



Figure 5.18: SEM images of F after 50 min etching in 30 wt. % aq. KOH at 80 °C. The images were taken from different positions on a single sample. The scale bar refers to all images. The second  $SiN_x$  layer was visible in form of plateaus on top of or within pyramids.

#### 5 Influence of Epitaxial Growth Conditions on Etch Rate

In summary, by decreasing the solution temperature, the selectivity between the etching of GaN and  $SiN_x$  was increased. To reach homogeneous etching, a high KOH temperature should be applied. On the other hand, etching at RT can be applied to utilize the high selectivity to intentionally stop the etch progress at the  $SiN_x$  or  $SiN_x/Al_{0.11}Ga_{0.89}N$ interface.



Figure 5.19: SEM images of F after 3 min etching in 30 wt. % aq. KOH at 70 °C and 5 h etching in 30 wt. % aq. KOH at RT. The images were taken from different positions on a single sample. The scale bar refers to all images. By combination of etching at 70 °C and RT, the etch process could be terminated at the second SiN<sub>x</sub> layer of F. For that, the temperature-dependency of plateau formation at the SiN<sub>x</sub> interface was applied.

# 5.5 Influence of TDs on Pyramid Tip Positions

## 5.5.1 CL Analysis of TDs and Correlation to Pyramid Pattern

Based on the determined etch kinetics of  $\mathbf{A}$  and  $\mathbf{D}$ , a ~fourfold difference in TD density had no influence on the GaN ER. Under the applied process conditions, the etch kinetics were independent from TD density. An influence of TDs on the preferential position of pyramid tips and valleys was, however, imaginable. To investigate that, CLM analysis of  $\mathbf{A}$  and  $\mathbf{C}$  was conducted after removal of LLO surface roughness by polishing (Figure 5.20). For that, enough GaN was removed from the surface of  $\mathbf{A}$  to take away both 2D GaN and SiN<sub>x</sub> entirely, which was reached with  $547 \pm 25 \text{ nm}$  material removal (mean  $\pm$  SDM, n = 5). 190  $\pm 21 \text{ nm}$  were removed from  $\mathbf{C}$  to supply a flat surface and prevent contrasts from LLO surface roughness (mean  $\pm$  SDM, n = 5). As no SiN<sub>x</sub> interface was present, a lower polishing depth was chosen. The thickness of removed GaN was determined by weighing of 6 inch GaN wafers before and after polishing.

During CLM, the positions of individual TDs could only be observed in case of  $\mathbf{A}$ . The high TD density of  $\mathbf{C}$  led to undistinguishable contrasts due to cluster formation of TDs. This had also been observed before during PLM analysis. In Figure 5.20, blue spots represent low CL emission, whereas in red areas the most light was emitted. The higher TD density of  $\mathbf{C}$ , which had been determined before to be  $> 4 \cdot 10^8 \text{ cm}^{-2}$ , resulted in a much finer distribution of contrasts during CLM analysis (Figure 5.20, right).

After CLM analysis, **A** was etched in 30 wt. % aq. KOH solution at 80 °C for 10 min. The identical surface section, which had been analyzed by CLM before etching, was investigated by SEM after etching (Figure 5.21). In the CLM image, the red dotted line marks a line-shaped dislocation cluster. Two red dotted circles mark individual TDs. The underlying functionality of CLM is based on the existence of additional non-radiative electron-hole recombination transitions at TDs. Hereby, the observation wavelength 365 nm equaled the band gap  $E_g$ . Dark areas stem from additional transitions (non-radiative or radiative at a different wavelength) at TDs as they compete against the direct band gap emission. The green oval shape in Figure 5.21 refers to a microscopic sample section with relatively high crystal quality, where no TD was located. This is represented by the bright CL emission.

The SEM image recorded after etching showed pyramid formation independently of TD positions (Figure 5.21, right). Also, the pyramid density formed by etching was significantly higher than the TD density. On an average, the 3D GaN layer of **A** had 1.3



Figure 5.20: CLM maps of A (left) and C (right) after surface polishing ( $\lambda = 365 \text{ nm}$ ). The contrasts correlate with the respective TD densities of  $1.3 \cdot 10^8 \text{ cm}^{-2}$  (A) and  $> 4 \cdot 10^8 \text{ cm}^{-2}$  (C). The higher TD density of C resulted in more finely distributed emission contrasts.



Figure 5.21: CLM image ( $\lambda = 365 \text{ nm}$ ) of GaN surface **A** before etching (left). By CLM, TDs were directly visible as dark spots, whereas defect-free crystal sections appeared bright. SEM image of identical surface section after etching in 30 wt. % aq. KOH solution at 80 °C for 10 min (right). The red dotted line and circles indicate positions of TDs. The green oval indicates an intact crystal section. No correlation was found between TDs and pyramid tip positions. Also, in some sections (i.e., in the top left part of both images), the pyramid density after etching was several times higher than the TD density of the material.

TDs per  $\mu$ <sup>2</sup>. The pyramid density especially in the upper left corner of Figure 5.21, right, was several times higher. This was in agreement with several literature reports, which have found no correlation between individual TDs and pyramid formation [89].

Two literature reports exist, in which local etch differences were attributed to dislocations. Chang and co-workers [87] observed crater formation over PSS side-walls. Due to the dislocation bending over PSS features, the lower local ER was claimed to stem from a lower TD density. Presumably, the epitaxial growth conditions were varied over the course of PSS growth in these experiments. The difference between 2D and 3D growth mode also had an influence on the ER in the experiments conducted during the course of this work. Thus, a systematic local difference in the ER could also be attributed to the growth conditions instead of the TD density. Wang and co-workers [94] reported a dependency of the local ER on TDs as well. It was claimed that crystal sections with a high dislocation density were etched at a higher ER. However, in their experiments, several dislocations were found also inside pyramid bodies. These results represent exceptions from the reported conclusion. Based on the reported TEM images, significant correlation was debatable. Under the conditions applied during the course of this work, no correlation existed between TDs and the positions of individual pyramids. On the one hand, CLM determined TDs did not influence the position of individual pyramid tips. This corresponded well to the observation that pyramid tips which were not caused by LLO surface damage were stable for at most 2 min etch time. On the other hand, the observed pyramid density was several times higher than the TD density.

# 5.6 Influence of TD Density on LLO Absorption

Next to the comparison of CLM images before etching and SEM images after etching, also the surface morphology before etching was investigated. After BOE pretreatment, a single surface section of a non-polished GaN sample **A** was analyzed by SEM and CLM (Figure 5.22).

Based on limited experimental data, a correlation was found between surface roughness caused by LLO and CL emission contrasts. The red circles in both images indicate disruptions in the surface observed by SEM. In these positions, fractures in the epitaxial surface were visible as ridges in the SEM image. When identical positions were analyzed by CLM, contrasts were found between dark and bright emission directly at the surface damage features. At first, these contrasts were attributed to directed refraction of emitted light at surface steps. To investigate the causal relationship, emission was investigated over several minutes of etching. This was carried out by PLM analysis of the identical emission wavelength 365 nm. Hereby, PLM showed the identical contrasts as CLM (Figure 5.23).

Already after 1 min etching in 30 wt. % aq. KOH at 70 °C, the entire LLO surface damage had been removed from the sample surface. Nevertheless, the contrasts in PL emission remained identical to the unetched surface. Thus, the LLO surface roughness did not direct the emission. *Instead, it is suggested that LLO light can be absorbed more efficiently in defect-rich GaN sections compared to intact regions*. As stated above, TDs add additional radiative and non-radiative transitions to the electronic structure of the material. The more efficient light absorption supposedly led to increased thermal GaN decomposition and thus an improved lift off result. On the other hand, more intact crystal regions remained intact. During removal of the substrate, these regions were separated mechanically rather than thermally. Sharp contrasts in CLM and PLM maps



Figure 5.22: SEM image of GaN surface A after BOE pretreatment (left) and CLM map ( $\lambda = 365 \text{ nm}$ ) of the same surface area (right). Red dotted circles indicate characteristic fractures in the GaN surface observed under SEM. These fractures correlated well with brightness contrasts in the CLM map.

correspond to sharp contrasts in TD density and moreover on lift off success. This implies that in the boundary region, cracks and steps in the material were created. In consequence, TDs eventually had an indirect influence on the etch behavior of GaN by affecting the local LLO surface damage. To gain overall understanding, further experiments are necessary. The importance of LLO damage and surface condition prior to etching will be in-depth discussed in chapter 6.

During PLM analysis, the positions of bright and dark spots remained identical up to an etch time of at least 5 min. Only the contrast decreased continually. The reason for that was light refraction at the rough pyramidal surface.



Figure 5.23: PLM images ( $\lambda = 365 \text{ nm}$ ) of identical GaN sample A surface section from 0 to 8 min etching in 30 wt. % aq. KOH solution at 70 °C. The scale bar refers to all images. The contrasts observed during PLM and CLM analysis were identical. After complete removal of the LLO damage morphology already after 1 min etch time, the observed contrasts remained identical. The contrasts were therefore not caused by LLO surface roughness but dislocation distribution. Blurring of the contrasts after longer etching occurred due to light refraction at the increasingly rough surface.

# 6 Pretreatment Strategies for Improved Etch Homogeneity

All experiments conducted so far showed linear etching once the  $SiN_x$  layer was crossed. Also, the degree of plateau formation was found to strongly depend on  $SiN_x$  coverage. Local differences in etch progress on the sample surface were investigated as well. Depending on the ratio of more and less etched surface sections, the combined average etch depth varied. Also, the LLO damage was suggested to lower the etch reproducibility. Two approaches for pretreatment prior to the actual etch process were investigated. The aim hereby was to homogenize the etch behavior on the entire wafer surface, which was monitored by the WLI determined  $S_q$  WIW roughness uniformity.

# 6.1 Room Temperature KOH Pretreatment

KOH etching at RT was able to remove the 2D GaN layer without crossing the SiN<sub>x</sub> interface. It was assumed that the creation of a flat and uniform surface could serve as a better starting point for further etching and thus increase reproducibility. To remove the initial LLO surface damage and 2D GaN, entire 6 inch wafers **A** were immersed in 30 wt. % aq. KOH solution at RT. The average etch depth was determined by weighing before and after 60 min etching. The reached material removal of  $220 \pm 25$  nm indicated that the SiN<sub>x</sub> interface had not yet been reached (mean  $\pm$  SDM, n = 5, Table 6.1). 60 min further processing led to  $300 \pm 18$  nm average material removal after a combined etch time of 120 min (mean  $\pm$  SDM, n = 5, Table 6.1). Subsequent SAT etching of all wafers with 30 wt. % aq. KOH at 90 °C was conducted to reach ~ 2000 nm material removal. SAT etching was thereby performed in 1 min steps with rinsing and drying of the wafers in between each etch cycle. Five reference SAT wafers without RT pretreatment thereby yielded  $2000 \pm 81$  nm average material removal after 9-10 min

(mean  $\pm$  SDM, n = 5, Table 6.2). RT pretreated wafers showed a remarkably higher variation of 2006  $\pm$  322 nm in SAT etch depth and 3-8 min in necessary etch time (mean  $\pm$  SDM, n = 5, Table 6.1).

RT KOH pretreatment thus led to an increased instead of decreased ER variation. The reason was found to be inhomogeneous crossing of the  $SiN_x$  layer. To visualize that, a rudimentary ER was calculated by division of the SAT material removal z (GaN) by the combined SAT process time and plotting against the RT material removal z (GaN) (Figure 6.1). Up to an average material removal of 304 nm during RT pretreatment, the resulting ER during SAT processing was equal to non-pretreated wafers.

When more material had been removed, the SAT ER increased rapidly. Wafers 3 and 5 had SAT ERs of  $469 \text{ nm min}^{-1}$  and even  $773 \text{ nm min}^{-1}$  after respective RT material removal depths of 312 nm and 323 nm. As mentioned earlier, at RT, the selectivity between GaN and the SiN<sub>x</sub> interface is higher than at  $90 \degree$ C. As a consequence, some

Wafer	1	2	3	4	5	$\mathrm{mean}\pm\mathrm{SDM^a}$
z (GaN) 60 min / nm	189	218	251	197	246	$220\pm25$
z (GaN) 120 min / nm	271	304	312	291	323	$300\pm18$
SAT etch time / min	8	8	3.25	7	3	$5.9\pm2.3$
$z ({\rm GaN}) {\rm total} /{\rm nm}$	1762	1894	1835	1899	2642	$2006\pm322$
SAT ER / nm min <sup>-1</sup>	186	199	469	230	773	$371\pm226$
WLI $\overline{S_q}$ / nm	582	580	631	616	808	$643\pm85$
WLI WIW	18%	13%	19%	14%	13%	$15\pm3\%$

**Table 6.1:** Material removal of five 6 inch GaN wafers **A** achieved by RT etching in 30 wt. % aq. KOH solution for 60 and 120 min; material removal after subsequent SAT etching in 30 wt. % aq. KOH solution at 90 °C. z (GaN) total [nm] refers to the combined weight loss of RT and SAT etching. Average RMS surface roughness  $\overline{S_q}$  and WIW non-uniformity were determined with 51 point WLI measurement of all wafers. a) n = 5.

Wafer	1	2	3	4	5	$\mathrm{mean}\pm\mathrm{SDM^a}$
SAT etch time / min	10	10	9	9	9	$9.4 \pm 0.5$
$z ~({\rm GaN}) \ / \ {\rm nm}$	2122	2069	1946	1915	1946	$2000\pm81$
SAT ER / $nm min^{-1}$	212	207	216	213	216	$213\pm3$
WLI $\overline{S_q}$ / nm	558	547	522	526	513	$533 \pm 17$
WLI WIW	5%	9%	9%	9%	8%	$7\pm2\%$

**Table 6.2:** Material removal of five reference 6 inch GaN wafers A achieved by SAT<br/>etching in 30 wt. % aq. KOH solution at  $90 \,^{\circ}\text{C. a}$ ) n = 5.



Figure 6.1: ER of five RT pretreated 6 inch GaN wafers during SAT processing in 30 wt. % aq. KOH solution at  $90 \,^{\circ}\text{C}$  versus material removal during pretreatment. The red line indicates the average SAT ER  $213 \pm 3 \text{ nm min}^{-1}$ , which was determined from five non-pretreated wafers during SAT etching under identical conditions. A high material removal during pretreatment led to a drastic increase in the subsequent SAT ER.

regions on the wafer had crossed the  $SiN_x$  layer already at RT. This led to a high ER during subsequent SAT etching. More slowly etched regions, on the other hand, still had the  $SiN_x$  interface and 2D GaN pyramids on the surface. This led to a decreased uniformity over the entire wafer surface. In other words, the inhomogeneity already existing during RT etching was multiplied during SAT etching (Figure 6.2).

Also, 51-point WLI analysis showed a higher WIW non-uniformity of  $15 \pm 3\%$  in case of RT KOH pretreatment compared to  $7 \pm 2\%$  reached by reference SAT etching (mean  $\pm$  SDM, n = 5). The average roughness  $\overline{S_q}$  thereby increased from  $533 \pm 17$  nm to  $643 \pm 85$  nm, which was caused by a high local variation in etch progress over the surface (mean  $\pm$  SDM, n = 5). Different heights of etch plateaus have a strong influence on  $S_q$ . Entire plateaus instead of pyramid valleys and tips were located below and above the average z-height of the surface.

This was confirmed by SEM (Figure 6.3, left). A significant local variation in the density and size of pyramids was observed. As pyramid size had been found to increase with material removal, the mean line of the surface was higher in case of small pyramids and lower in case of large pyramids. For comparison, the pyramid size distribution was more narrow, when no pretreatment had been applied beforehand (Figure 6.3, right).



Figure 6.2: Schematic difference in etch uniformity during SAT etching between wafers without (left) and with pretreatment in 30 wt. % aq. KOH solution at RT (right). Blue arrow sizes represent local differences in the ER, which is especially increased when the entire  $SiN_x$  layer was removed during pretreatment. Compared to that, the ER of non-pretreated wafers was more homogeneous.



Figure 6.3: SEM image of GaN sample A after 120 min pretreatment in 30 wt. % aq. KOH at RT and subsequent SAT etching at 90 °C (left). SEM image of reference GaN sample A after 9 min SAT etching in 30 wt. % aq. KOH solution at 90 °C (right). The pyramid size distribution was more homogeneous without pretreatment of the samples at RT. The varying local removal of the SiN<sub>x</sub> interface during RT pretreatment multiplied the non-uniformity during subsequent SAT etching at high temperature.

In summary, pretreatment in 30 wt. % aq. KOH for 120 min at RT did not lead to an improved etch uniformity. Instead, the higher impact of material-variation during etching at RT compared to 80 °C caused an even higher local variation in etch depth on the surface. Whereas in some sections of the surface, the SiN<sub>x</sub> interface had been already crossed, other sections still had  $SiN_x$  and 2D GaN pyramids on the surface. As soon as SAT etching at 90 °C set in, the local ER variation was again drastically increased. Exposed 3D GaN was etched at a high ER, whereas in other regions the  $SiN_x$  plateau still had to be overcome. Instead of the expected uniformity increase by LLO damage removal, the material variation was multiplied by RT KOH pretreatment. At RT, surface damage caused even higher etch selectivity than at elevated temperature.

# 6.2 Mechanical Surface Polishing

Mechanical polishing of GaN wafers was conducted with two different polishing times of 48 s and 128 s. Thereby, the shorter time was applied on bulk GaN **C** to produce a uniform and preconditioned surface without removing a lot of material. Samples with a SiN<sub>x</sub> layer (**A**, **D**, **E**) were addressed with the longer polishing time to remove both 300 nm 2D GaN and the entire SiN<sub>x</sub> layer. Mass and height of the removed GaN material were determined by weighing before and after polishing (Table 6.3). 48 s polishing of **C** yielded an average removal depth of  $190 \pm 21$  nm, whereas the longer polishing time yielded  $547 \pm 25$  nm material removal in case of **A** (mean  $\pm$  SDM, n = 5). By AFM, the  $R_q$  surface roughness was determined before and after polishing of **A** as 24.8 and 1.1 nm, respectively (Figure 6.4). Both process times were able to achieve a shiny surface showing no visible remaining surface damage from LLO (Figure A.3).

Polishing time / s	m (GaN) on $6$ inch wafer / mg	z (GaN) / nm
48	$21\pm2$	$190\pm21$
128	$59\pm3$	$547\pm25$

**Table 6.3:** Weight loss of 6 inch GaN wafers and calculated average removal achieved by surface polishing for 48 s (**C**) and 128 s (**A**). The data is presented as mean  $\pm$  SDM, n = 5 wafers. For both polishing times, the material removal showed a low percentage variation from wafer to wafer, which is represented by the SDM.



**Figure 6.4:** AFM images of GaN surface **A** before (left) and after polishing in alkaline slurry for 128 s (right). The calculated  $R_q$  values were 24.8 nm before and 1.1 nm after polishing.

# 6.2.1 Comparison of Etch Kinetics after Polishing

After polishing, the ERs of A and C were compared to non-polished samples in 30 wt. %aq. KOH solution at 80 °C (Figure 6.5). The material removal reached by polishing was set as the y-interception in the respective plots. Thereby, the actual depth of transitions in the epitaxial layer stack was identical between polished and non-polished samples. GaN polishing was only possible on a wafer base. Thus, the samples used for comparison between polished and non-polished A did not stem from an identical wafer and comprised a non-determinable material variation. This must be kept in mind during the following discussion. Polishing of A and C led to an ER increase of 88% and 500% compared to the non-polished samples, respectively (Table 6.4). The total thickness of bulk GaN C was  $3\,\mu\text{m}$ . The saturation of C after  $1500\,\text{nm}$  material removal was caused by approaching of the lot metal in the valleys between the pyramids. Also, the ER of  $\mathbf{A}$  saturated after 1500 nm. Although the total thickness of the GaN layer stack was higher, the layer stack was only homogeneous until 3000 nm. To remain inside this layer, only the etch kinetics up to 1500 nm average etch depth were relevant. Higher average material removal values than 1500 nm were not considered anymore and are printed grey in Figure 6.5. The ERs of A and C were equally determined between 600-1500 nm material removal. Thereby, both the higher initial ER due to undefined surface states and ER saturation by approaching the lot metal were circumvented.

Sample	ER without polishing / $nm min^{-1}$	ER with polishing / $\rm nmmin^{-1}$
Α	$338 \pm 30 \ (11 \% \text{ SDM})$	$655 \pm 108 \ (16 \% \text{ SDM})$
$\mathbf{C}$	$147 \pm 17 \ (12 \% \text{ SDM})$	$890 \pm 91 \ (10 \% \text{ SDM})$

**Table 6.4:** ER of GaN samples **A** and **C** determined from the linear section of etch kinetics (plot above) in 30 wt. % aq. KOH solution at 80 °C. Errors were determined as mean  $\pm$  SDM,  $n \geq 3$ .

#### 6.2.2 Increased Etch Rate by Development of $(000\overline{1})$ Coverage

As only the surface was preconditioned by polishing, a long-ranging memory effect into the material was not expected. To explain the reason for the ER increase, the anisotropic character of GaN etching must be taken into account. *Pyramid formation* generally occurs due to a larger ER of the horizontal (0001) crystal facet compared to the  $\{10\overline{11}\}$  pyramid side facets. This is mandatory for the observed anisotropic etching and is expressed by

$$ER_{(000\overline{1})} > ER_{\{10\overline{11}\}}$$
 . (6.1)

Further on, the total ER is a combination of  $(000\overline{1})$  and  $\{10\overline{11}\}$  etching.

$$ER_{total} = A_{(000\overline{1})} \cdot ER_{(000\overline{1})} + A_{\{10\overline{11}\}} \cdot ER_{\{10\overline{11}\}}$$
(6.2)

Hereby,  $A_{(000\overline{1})}$  and  $A_{\{10\overline{1}\overline{1}\}}$  refer to the total area of the individual crystal facets present on the surface. After polishing, the initial surface was 100 % covered with (000\overline{1}) crystal facet due to effective removal of damage and LLO caused surface roughness. The high  $A_{(000\overline{1})}$  area caused a higher initial  $ER_{total}$ , which saturated with increasing material removal. During the etch process, also  $A_{\{10\overline{1}\overline{1}\}}$  increased due to pyramid formation. On the other hand, the LLO surface roughness of the non-polished sample provided a rough surface leading to a higher  $A_{\{10\overline{1}\overline{1}\}}$  coverage already in the early stage of etching. To give evidence to this mechanism, SEM analysis of polished and non-polished **C** was performed over several minutes of etching in 30 wt. % aq. KOH solution (Figure 6.6). The solution temperature was thereby decreased from 80 °C to 60 °C to lower the ER and achieve reasonable sample taking intervals.



Figure 6.5: ICP-OES determined material removal of non-polished and polished GaN samples A (left) and C (right) during etching in 30 wt. % aq. KOH at 80 °C. The data is presented as mean  $\pm$  SDM, n  $\geq$  4. The color codes of the epitaxial layer stacks are identical to Figures 5.2 and 5.12. It was removed for better visibility of the data. After polishing, the ERs of A and C were significantly higher compared to the identical material etched without foregoing polishing.

Visual comparison of the pyramid coverage showed that already after 1 min etching > 80 % of the non-polished surface was covered with  $\{10\overline{11}\}$  facets. With increasing etch time, the pyramids evolved larger, which corresponded well to the previously discussed experiments (see section 5.3). The (000 $\overline{1}$ ) coverage of polished wafers was larger at all times and especially during initial etching. The longer etching was conducted, the larger pyramids evolved. Thereby, the (000 $\overline{1}$ ) coverage decreased and with it  $ER_{total}$  decreased as well. Without polishing, linear etching after 2 min was obvious as the entire surface was covered with pyramids (Figure 6.5). This led to a constant total surface area made up by  $\{10\overline{11}\}$  facets and thus a constant  $ER_{total}$  after Equation 6.2. In case of polished samples, the steadily changing (000 $\overline{1}$ ) coverage led to an equally changing crystal facet ratio  $A_{(000\overline{1})}:A_{\{10\overline{11}\}}$  and total surface area. Both the latter parameters influence the ER. Based on these theoretical and experimental considerations, the long-ranging effect of surface polishing on the GaN ER could be explained in detail.

## 6.2 Mechanical Surface Polishing



Figure 6.6: SEM images of non-polished (0 min, 1 min, etc.) and polished (P 0 min, P 1 min, etc.) GaN samples C before and after etching for 1-5 min in 30 wt. % aq. KOH at 60 °C. The (0001) surface coverage was higher on the polished GaN surface at all times. This led to an increased ER. On the other hand, the LLO surface roughness caused quick saturation of the surface with {1011} pyramids and thus a constant and lower ER.

# 6.2.3 Increased Etch Reproducibility by LLO Damage Removal

In previously discussed experiments (chapter 5), it was necessary to use adjacent sample pieces of an identical wafer. Only in this way, sufficient reproducibility was achieved to resolve the differences in the epitaxy stacks. As soon as different regions on an

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epitaxial wafer were considered and etched under identical conditions, the SDM was higher. The expected improved reproducibility achieved by polishing was further investigated. For that, eight individual samples **C** from multiple positions on one wafer were etched in 30 wt. % aq. KOH solution at 60 °C. For comparison, eight non-polished GaN samples **C** were included in the experiment as well. In the extensive study, a total number of 160 data points were analyzed by ICP-OES. The etch kinetics were thereafter determined by linear regression (Figure 6.7).

The ER after polishing had a value of  $268 \pm 26 \text{ nm min}^{-1}$  compared to  $66 \pm 26 \text{ nm min}^{-1}$ (mean  $\pm$  SDM, n = 8) without polishing. The ER was thereby determined between 2.5 min and 5.5 min. Next to the ~ 300 % increase in ER, the relative SDM decreased from 28 % to 10 % (n = 8). Thus, LLO surface roughness removal achieved by polishing prior to etching brought a significant benefit in terms of etch reproducibility (for visualization of the etch kinetics of 8 single experiments, see Figure A.4).

The impact of LLO surface damage or surface roughness was investigated and analyzed for the first time. It was found to be the most important parameter in control of ER variation over the wafer surface. It's removal by polishing could effectively be applied to increase etch reproducibility, which is of utmost importance for industrial processing.



Figure 6.7: ICP-OES determined etch kinetics of non-polished and polished GaN samples C during etching in 30 wt. % aq. KOH solution at 60 °C. The data is presented as mean  $\pm$  SDM, n = 8. Both the increased ER as well as the significantly decreased relative error are visible. For increasing the etch reproducibility, mechanical polishing is a very powerful tool.
#### 6.2.4 Productive Application of Mechanical Surface Polishing

Based on the increased etch reproducibility achieved by polishing, two potential processes for productive application were investigated. The aim hereby was to propose two different promising approaches to implement polishing into the preliminary process flow. On a basis of 5 wafers per variation, statistical data was obtained. In one approach, mechanical polishing was combined with tank tool etching at RT. Hereby, whole wafers were immersed in slightly stirred KOH solution. Etching at RT was chosen to utilize the increased ER of the polished surface. The lower temperature was intended to decrease an effect of temperature variation on the wafer. The second process combined polishing and subsequent SAT etching at 60 °C. Both processes were compared to reference SAT processing of non-polished wafers at 90 °C.

#### 6.2.4.1 Polishing and Tank Etching at RT

Five 6 inch wafers **A** were polished to remove both 2D GaN and the SiN<sub>x</sub> interface (Table 6.5, top). By polishing and a combined tank etch time of 80 min in 30 wt. % aq. KOH, an average material removal of  $1739 \pm 75$  nm was reached (mean  $\pm$  SDM, n = 5, Table 6.5, middle). Thereby, the tank etch time was identical for all wafers. Reference GaN wafers processed by SAT etching at 90 °C achieved  $2000 \pm 81$  nm material removal after 9-10 min (Table 6.2, top). The new combined process yielded a similar relavite SDM of the material removal, but kept an identical processing time for all wafers. As a consequence, the etch wafer-to-wafer homogeneity was increased by polishing and RT etching compared to the reference SAT process.

When not the difference between wafers was considered, but the uniformity over a single wafer, the combined polishing and tank etch process showed superior uniformity. WLI

Wafer	1	2	3	4	5	$\mathrm{mean}\pm\mathrm{SDM^a}$
z (GaN) after polishing / nm	471	435	449	421	432	$446 \pm 16$
z (GaN) 80 min / nm	1759	1727	1778	1603	1826	$1739\pm75$
$\overline{\text{WLI } \overline{S_q}} / \text{nm}$	521	522	507	475	509	$506 \pm 17$
WLI WIW	7%	4%	4%	4%	4%	$5 \pm 1 \%$

**Table 6.5:** Material removal of five 6 inch GaN wafers A achieved by polishing as well<br/>as subsequent tank tool etching in 30 wt. % aq. KOH solution at RT for<br/>80 min. a) n = 5.

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measurement was conducted to determine  $\overline{S_q}$  and WIW (Table 6.5, bottom). The absolute surface roughness  $\overline{S}_q$  achieved by the alternative process was slightly lower with a value of  $506 \pm 17$  nm (mean  $\pm$  SDM, n = 5). Reference SAT wafers processed at 90 °C reached  $533 \pm 17$  nm (mean  $\pm$  SDM, n = 5, Table 6.2, bottom). The lower  $\overline{S_q}$  after polishing and tank etching was caused by the flat (0001) surface, which was present directly after the polishing depth of  $446 \pm 16$  nm (mean  $\pm$  SDM, n = 5). Compared to that, the non-polished samples had a flat plateau during crossing of the SiN<sub>x</sub> layer after only ~270 nm material removal. During the course of additional ~180 nm etch depth in case of the non-polished samples, the pyramids on the on the surface could evolve larger and also thereby yield a higher  $\overline{S_q}$  roughness compared to the polished GaN.

The WLI WIW improved from  $7 \pm 2\%$  to  $5 \pm 1\%$  by the new process design (mean  $\pm$  SDM, n = 5, Table 6.2, Table 6.5). This showed an increase in surface homogeneity over the wafer caused by the removal of radius-dependent LLO damage prior to etching. In this way, the light emission characteristics of different final LED chips from different regions on a wafer can be effectively homogenized.

#### 6.2.4.2 Polishing and SAT Etching at 60 °C

Next to tank etching at RT, also a combination of polishing and SAT etching at 60 °C was investigated. The KOH temperature during SAT etching was decreased from 90 °C to 60 °C to slow down the ER. Generally, etch processes with a duration of <1 min would lack control due to often undefined conditions at process start or end (e.g., wetting or drying effects). Polishing led to an average material removal of  $440 \pm 12 \text{ nm}$  (mean  $\pm$  SDM, n = 5, Table 6.6, top). Subsequently, a uniform SAT etch time of  $3 \cdot 1 \text{ min}$  achieved an average material removal of  $1864 \pm 60 \text{ nm}$  (mean  $\pm$  SDM, n = 5, Table 6.6, top). Subsequently, a uniform SAT etch time of  $422 \pm 6 \text{ nm}$  compared to SAT etching with a  $\overline{S_q}$  of  $533 \pm 17 \text{ nm}$  (mean  $\pm$  SDM, n = 5, Table 6.2, Table 6.6). The necessary etch time was identical for all wafers after polishing. The lower  $\overline{S_q}$  roughness was at first attributed to the flat surface after  $440 \pm 12 \text{ nm}$  polishing depth, as it was argued in section 6.2.4.1. Therefore, further etching for  $2 \cdot 15 \text{ s}$  was applied. A total material removal of  $2290 \pm 90 \text{ nm}$  was reached (Table 6.6). The height difference between polishing depth and SiN<sub>x</sub> layer in non-polished samples was compensated by the additional etch steps.

Wafer	1	2	3	4	5	$\mathrm{mean}\pm\mathrm{SDM^a}$
$\overline{z(\text{GaN})}$ after polishing / nm	426	432	449	431	459	$440 \pm 12$
z (GaN) 3.0 min / nm	1766	1832	1900	1882	1939	$1864\pm60$
WLI $\overline{S_q}$ 3.0 min / nm	419	424	432	421	415	$422\pm 6$
WLI $WIW$ 3.0 min	5%	6%	5%	5%	6%	$5\pm1\%$
z (GaN) 3.5 min / nm	2162	2225	2331	2309	2424	$2290\pm90$
WLI $\overline{S_q}$ after 3.5 min / nm	384	379	399	385	395	$388 \pm 7$
WLI $WIW$ 3.5 min	7%	7%	5%	8%	6%	$7 \pm 1 \%$

**Table 6.6:** Material removal of five 6 inch GaN wafers **A** achieved by polishing and subsequent SAT etching for 3.0 or 3.5 min in 30 wt. % aq. KOH solution at 60 °C. Average RMS surface roughness  $\overline{S_q}$  and WIW non-uniformity were determined with 51 point WLI measurement of all wafers. a) n = 5.

Instead of the expected higher surface roughness, however,  $\overline{S_q}$  further decreased to  $388 \pm 7 \,\mathrm{nm}$  (mean  $\pm$  SDM, n = 5, Table 6.6, bottom). SEM analysis of the wafers showed plateau formation (Figure A.5). Subsequent FIB cutting and cross-section SEM analysis of the plateau z-height proved that the layer transition between 3D GaN and 2D-2 GaN occurred at that point in the epitaxial stack (Figure A.6). With the used epitaxial design, the surface roughness reached by SAT etching of polished wafers at 60 °C could not reach a  $\overline{S_q}$  comparable to the 90 °C reference process. This was caused by the slower saturation of the surface with  $\{10\overline{11}\}$  pyramids and plateau formation at an epitaxial layer transition. For productive application, the 3D GaN thickness must therefore be increased by ~ 300 nm.

Regarding the etch uniformity, the percentage SDM of z (GaN) achieved over five wafers was reduced from 4.1% to 3.2%. Simultaneously, the WIW non-uniformity was improved from  $7 \pm 2\%$  to  $5 \pm 1\%$  at the same material removal (mean  $\pm$  SDM, n = 5). By novel combinations of polishing and wet-chemical etching, the uniformity in surface roughness and etch reproducibility could be significantly increased.

In conclusion, it was shown that LLO damage was the main impact causing inhomogeneous etching both from wafer to wafer and on the surface of a single wafer. Pretreatment of GaN wafers at RT was conducted to terminate etching selectively at the  $SiN_x$  interface. Thereby, the LLO damage could be successfully removed. However, the initial surface damage transcribed into inhomogeneous crossing of the  $SiN_x$  interface. As soon as subsequent SAT etching at elevated temperature set in, the local ER differences were even more increased, which was confirmed by measurement of aver-

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age material removal and surface roughness uniformity. Polishing, on the other hand, allowed for a homogeneous processing time over 5 wafers. Also, a superior roughness uniformity could be reached. Two approaches for the implementation of polishing into the previous SAT process flow were presented and analyzed on a statistical basis. Both showed promising homogenization of the etch process.

# 7 Influence of Etch Process Parameters on Etch Rate

Next to material-dependent parameters, also the ability to control the ER by the process conditions has been reported multiple times in literature. The influence of etch temperature, KOH concentration and solution agitation was investigated with the current material system. Polished GaN  $\mathbf{C}$  was used as a standard sample material. Thereby, the high material reproducibility could be utilized for unprecedented resolution of minor ER changes caused by process control.

# 7.1 Variation of KOH Concentration

At 60 °C solution temperature, the KOH concentration was varied between 0 wt. % and 50 wt. %. Polished GaN samples **C** were immersed in the respective solutions. By ICP-OES, the etch kinetics were determined. The ER was acquired by the first order fit of effectively linear sections in the kinetics between 900 nm and 1600 nm average material removal z (GaN) (Figure 7.1, left). As mentioned earlier, the material removal from 0 nm to 900 nm was not considered due to the slow development of pyramid facets. The material removal range upwards from 1600 nm was not considered because the valleys in between pyramids approached the lot metal at that point.

Between 0 wt. % and 23 wt. % aq. KOH, a steady ER increase was observed. After a peak at 23 wt. %, the ER decreased again. At 50 wt. % KOH, the ER had a value of only  $20 \pm 4$  nm min<sup>-1</sup> (mean  $\pm$  SDM, n = 3). The exact peak position was investigated by a more finely resolved KOH concentration variation between 20 wt. % and 26 wt. % (Figure 7.1, right). At 23 wt. %, the highest ER of  $318 \pm 15$  nm min<sup>-1</sup> was achieved. For optimum process control, the ER maximum at 23 wt. % is the ideal set point. At



Figure 7.1: ICP-OES determined ER of polished GaN samples C in 0 wt. % - 50 wt. % (left) and 20 wt. % - 26 wt. % aq. KOH solution at 60 °C (right). The data is presented as mean  $\pm$  SDM, n  $\geq$  3. The y-axis was kept identical in both plots to ensure comparability of the data. The maximum ER was found at 23 wt. % aq. KOH.

this point, small changes in the KOH concentration into each direction only lead to a slightly decreased ER. Compared to that, a set point at 35 wt. % would cause an ER increase towards lower and a decrease towards higher KOH concentrations.

Also during etching of polished **C** at RT, a peak at 24 wt. % KOH was found in the studies of Maren Teresa Kuchenbrod [109] resulting in an ER of  $24 \pm 2 \text{ nm min}^{-1}$ . For MBE grown GaN on (111) Si substrates, Palacios and co-workers [81] reported an ER maximum at ~6 mol L<sup>-1</sup> aq. KOH, which equals ~27 wt. %.

To show the importance of surface polishing for the discussed experiment, Figure A.7 contains the ICP-OES determined ER of non-polished GaN **A** etched in 20-26 wt. % KOH solution at 80 °C. In that experiment, material-variation due to inhomogeneous LLO surface roughness overwhelmed the slight ER changes between 20 and 26 wt. % KOH, so that no conclusion could be drawn out of that experiment. With polishing, on the other hand, the exact peak position could be determined to be 23 wt. %.

## 7.2 Variation of Solution Temperature

To determine the influence of solution temperature on the GaN ER, polished samples C were etched in 30 wt. % aq. KOH solution. The temperature was varied between 22 °C and 80 °C. Again, the ER was determined in the effectively linear etch kinetics section between 900 nm and 1600 nm z (GaN) (Figure 7.2, left. For tabular data see Table A.3.).

The ER increased exponentially with temperature, which agreed with literature reports [35, 47, 81, 94]. A threshold, under which no etching occurred, was not found. Even at RT, an ER of  $12 \pm 1 \text{ nm min}^{-1}$  was measured from 25 min to 55 min etch time (mean  $\pm$  SDM, n = 3). The highest ER was observed at 80 °C solution temperature at a value of  $868 \pm 35 \text{ nm min}^{-1}$  (mean  $\pm$  SDM, n = 3).

Based on the determined ER values, the activation energy  $E_a$  of polished GaN C was determined. For zero-order reactions, the Arrhenius equation is given as

$$k = A e^{\frac{-\mathbf{L}_a}{k_B T}} \quad . \tag{7.1}$$

Hereby, k is the rate constant, A a pre-exponential factor,  $E_a$  the activation energy of the reaction,  $k_B$  the Boltzmann constant and T the absolute temperature in K [95].



Figure 7.2: ICP-OES determined ER of polished GaN samples C in 30 wt. % aq. KOH solution at temperatures from 22 °C to 80 °C (left, mean  $\pm$  SDM, n = 3, for tabular data see Table A.3). Arrhenius plot of the identical samples with linear fit for determination of E<sub>a</sub> (right, mean  $\pm$  SDM, n = 3). Fit function ln (ER) =  $(-7773 \pm 505)T^{-1} + (29 \pm 1)$ ; R-Square = 0.979.

#### 7 Influence of Etch Process Parameters on Etch Rate

This equation can be equivalently written as

$$ln(k) = ln(A) - \frac{E_a}{k_B} \cdot \frac{1}{T}$$
 (7.2)

Thus, the y-intercept of the fitted linear Arrhenius plot equals ln(A) (Figure 7.2, right). The slope is equal to  $-\frac{E_a}{k_B}$ . With that,  $E_a$  of polished GaN C was determined.

$$E_a = 0.67 \pm 0.04 \, eV \tag{7.3}$$

The error was hereby determined from three individually etched samples per solution temperature. The determined activation energy corresponded well to several literature reports for other GaN material systems, in which  $E_a$  values between 0.13 eV and 0.78 eV were calculated [35, 47, 81, 94]. The obtained activation energy clearly showed that the GaN etch reaction was kinetically controlled under the applied process conditions. Diffusion controlled reactions are typically below 0.2 eV [113].

The etch setup used for ICP-OES analysis of the reaction kinetics comprised magnetic stirring. This was needed to provide sufficient convection for a reproducible sample taking for ICP-OES analysis. Under the here applied process conditions, samples etched without convection had the identical material removal as samples etched under stirring. *Solution agitation had no impact on the GaN ER.* 

The processing temperature should be kept high to decrease the impact of inhomogeneities in the epitaxial layer stack on the ER. Otherwise, no influence on the etch reproducibility exists. For productive processing, however, the temperature uptake of the wafer especially in the initial etch period must be considered. Hereby, the KOH medium flow shows influence as decreased solution-wafer contact decreases the etch temperature and therefore the etch temperature.

In conclusion, the previously reported ER peak at about half the maximum KOH concentration was confirmed. The precise position was clarified to be at 23 wt. % aq. KOH. For maximum process control, this peak position is the ideal set point due to a minimum ER change in both directions of KOH concentration. For the conducted experiments, the availability of polished GaN **C** was of utmost importance. It was shown that the identical experiment conducted with unpolished GaN was meaningless due to material variation caused by inhomogeneous LLO surface roughness. Also, an exponential dependency of the ER on the solution temperature was confirmed.

activation energy of the etch reaction was determined to be  $0.67 \pm 0.004 \,\text{eV}$ . Local differences in KOH concentration due to medium circulation had no impact due to kinetic hindrance of the reaction. For low KOH concentrations or PEC experiments, however, diffusion limitation does play a role, which has been reported before [103, 114, 115].

# 8 Molecular Etch Mechanism and Directional Anisotropy

Based on the observed material- and process-influences on the GaN etch kinetics, the process was investigated on the atomic level. First, the stoichiometric etch reaction was analyzed under the applied process conditions. Further on, the underlying reason for anisotropic etching was examined. Finally, the electronic influence on the ER is discussed.

## 8.1 Substitution Mechanism under NH<sub>3</sub> Formation

Depending on the process conditions, several different reaction formulas had been reported [83, 89, 94, 104, 105]. These could be separated into formal substitution mechanisms without participation of electron transfer and redox mechanisms. Due to the electronegativity difference between Ga and N, the bond character is mainly ionic. As a consequence, Ga has the formal oxidation state +3. N has the formal oxidation state -3. In all reported mechanisms, the Ga charge remained identical. Therefore, the Ga oxidation discussed in foregoing literature must rather be described as a substitution reaction of Ga-N bonds with Ga-O bonds. Even if a redox mechanism was stated, the formation of gaseous H<sub>2</sub> or N<sub>2</sub> was suggested. In that case, H<sup>+</sup> was supposed to be reduced to H<sub>2</sub>, whereas N<sup>3-</sup> was oxidized to N<sub>2</sub>.

$$6 \text{ H}^+ + 6 e^- \rightarrow 3 \text{ H}_2$$
 (8.1)

$$2 N^{3-} \rightarrow N_2 + 6 e^-$$
 (8.2)

#### 8 Molecular Etch Mechanism and Directional Anisotropy

Under PEC etch conditions, electron-hole pairs are generated in the crystal by optical excitation of electrons. Due to surface band bending, in n-GaN, electrons drift into the bulk crystal, whereas holes accumulate at the GaN-solution interface [116]. As u-GaN used during the course of this study was also slightly n-doped, the same phenomenon was adapted. The holes taking part in the reaction serve as an oxidation agent, which implies influence on the etch mechanism. However, in case of electro-less and dark etching of GaN, no hole implantation occurs. Thus, a mechanism without redox character was feasible. All reported mechanisms without redox character contained the formation of  $NH_3$ .

#### 8.1.1 Characterization of Reactants and Reaction Products

#### 8.1.1.1 Absence of Gaseous Reaction Products

The reactants as well as the reaction products were investigated for the clarification of the reaction mechanism. A 6 inch GaN wafer **A** was pretreated with BOE solution to remove LLO residues (Ga and GaO<sub>x</sub>), which would eventually have led to side reactions. Subsequently, the wafer was immersed in 30 wt. % aq. KOH solution at 80 °C. After crossing of the SiN<sub>x</sub> interface, an ER of  $338 \pm 30 \text{ nm min}^{-1}$  had been determined before (mean  $\pm$  SDM, n = 3, Figure 5.2). This ER translated into 0.425 mg min<sup>-1</sup>. The amounts of formed N<sub>2</sub> and H<sub>2</sub> gas would then have come to  $2.54 \cdot 10^{-6} \text{ mol min}^{-1}$  and 7.61  $\cdot 10^{-6} \text{ mol min}^{-1}$ , respectively. For the calculation of the latter amounts, it was suggested that in case of a redox reaction, per formula unit GaN, 0.5 units N<sub>2</sub> and 1.5 units H<sub>2</sub> should be formed.

Compared to GaN, the ER of Si exposed on the wafer's side wall was determined by ICP-OES to be  $1185 \pm 99 \text{ nm min}^{-1}$  (mean  $\pm$  SDM, n = 7). Whereas the ER of Si was therefore three times as high as the ER of GaN, the area of Si was much smaller on the side wall than the GaN area of the entire 6 inch wafer. At the wafer side walls, H<sub>2</sub> bubble formation was clearly observed. No bubble formation was, however, found on the wafer surface. From that, it was concluded that neither H<sub>2</sub> nor N<sub>2</sub> were formed during the GaN etch reaction.

#### 8.1.1.2 NH<sub>3</sub> Detection by pH Change above Solution

Further on, two separate experiments were conducted to detect  $NH_3$  formation during etching. In strongly alkaline KOH solution, eventually formed ammonia would be present in its deprotonated form  $NH_3$  instead of  $NH_4^+$ . This would decrease solubility and lead to outgassing. Above the KOH solution, a wet pH indicator stripe was placed. Three separate experiments contained 20 mL 30 wt. % aq. KOH with a polished GaN sample **C** inside the solution. Also, three control experiments did not contain GaN but only KOH solution. Subsequently, the vials were closed and slowly heated to 50 °C.

During heating, the pH indicator stripes indicated a pH change from 7 to 12 above the KOH samples containing GaN (Figure 8.1, right). The negative control experiments, which only contained KOH but no GaN, remained at pH 7 (Figure 8.1, left). The formation and evaporation of  $NH_3$  in case of GaN etching caused the pH increase. KOH did not evaporate from the solution.



Figure 8.1: Images of wet pH indicator stripes above 20 mL 30 wt. % aq. KOH solution without (left) and with (right) polished GaN samples C in solution. The closed vials were heated slowly to 50 °C leading to a pH increase above solution only when GaN was etched. This hinted at the development of  $NH_3$ , which evaporated.

#### 8.1.1.3 NH<sub>3</sub> Detection by Berthelot Reaction

Next to pH measurement above the solution, the Berthelot reaction was applied as a second method to detect  $NH_3$  formation selectively. In its first step, the Berthelot reaction describes the oxidation of  $NH_3$  by NaOCl to  $NH_2$ Cl [110].

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH$$
 (8.3)

Subsequently, NH<sub>2</sub>Cl reacts with thymol to a blue indole dye.



The control experiment (Entry 1), which contained only NaOCl and thymol, showed a colorless aq. KOH phase and a brown organic (org.) thymol phase on top. The appearance of all Entries are summarized in Table 8.1 and Figure 8.2. To the reference system (Entry 1), 100 µL 26 wt. % NH<sub>3</sub> were added in Entry 2, which led to a yellowgreen color of the aq. phase and a blue discolored org. phase (Figure 8.2, Entry 2). To remove the eventual influence of silicon or other metallic layers in the chip stack of GaN sample **A**, pieces (Figure 8.2, Entry 3) and grinded powder of a 2 inch bulk GaN wafer (Figure 8.2, Entry 4) were added to the KOH solution containing NaOCl and thymol. This led to a yellow discoloration of the aq. phase, whereby the thymol phase remained brown. Etching of the bulk GaN wafer, however, proceeded at a low ER. The reason for that was, that the entire N-face had aready been fully covered by  $\{10\overline{11}\}$  pyramids prior to etching.

To obtain a higher ER, a polished sample  $\mathbf{A}$  with  $2 \text{ cm}^2$  initial  $(000\overline{1})$  area was etched (Figure 8.2, Entry 5). This experiment showed yellow and blue discoloration of the aq.

8.1	Substitution	Mechanism	under	$NH_3$	Formation
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Entry	V (NH <sub>3</sub> ) / μL	GaN/Si sample	App. aq. phase	App. org. phase
1	-	-	Colorless	Brown
2	100	-	Yellow	Blue
3	-	2 inch GaN pieces	Yellow	Brown
4	-	2 inch GaN grinded	Yellow	Brown
5	-	polished GaN ${f A}$	Yellow	Blue
6	-	Si substrate	Colorless	Brown

Table 8.1: Berthelot reaction experiments for NH<sub>3</sub> detection in aq. KOH at 80 °C. All Entries contained 20 mL 30 wt. % aq. KOH, 100 µL NaOCl solution (14 wt. % active Cl<sub>2</sub>) and a spatula tip thymol. Entries 1-2 represent control experiments without (Entry 1) and with (Entry 2) directly added NH<sub>3</sub>. Entries 3 and 4 contained grinded 2 inch bulk GaN substrate in form of pieces (Entry 3) or in grinded form (Entry 4). In Entry 5, a polished 2 cm<sup>2</sup> GaN sample A was etched. Entry 6 comprised a 2 cm<sup>2</sup> Si substrate piece. The visual appearance (App.) of all experiments is shown in Figure 8.2.



Figure 8.2: Images of Berthelot reaction Entries 1-6 for detection of NH<sub>3</sub> in aq. KOH solution at 80 °C. All Entries contained 20 mL 30 wt. % aq. KOH, 100 µL NaOCl solution (14 wt. % active Cl<sub>2</sub>) and a spatula tip thymol. Entry 1 contained no further substances, whereas to Entry 2 100 µL 26 wt. % NH<sub>3</sub> were added. The remaining Entries contained pieces (3) and powder (4) of a bulk u-GaN substrate wafer,  $2 \text{ cm}^2$  polished **A** (5) and  $2 \text{ cm}^2$  Si substrate piece (6). Entry 5 showed the same appearance as Entry 2, which gave evidence to NH<sub>3</sub> formation during GaN etching.

and org. phase, respectively. The appearance corresponded well to Entry 2. The control experiment comprising only Silicon (Figure 8.2, Entry 6) revealed that Si etching did not contribute to the discoloration (Figure 8.2, Entry 6). In conclusion, the blue color observed in Entry 5 must stem from the indole-compound. To achieve the blue color, a nitrogen bridge in between two benzene rings is necessary, which must stem from ammonia formed during GaN etching. Confirmed  $NH_3$  formation was the consequence of that.

In summary, it was proven in two separate experimental approaches that  $NH_3$  was formed as a reaction product under the applied etch conditions. Also, in a preliminary study, the absence of gaseous reaction products (i.e.,  $H_2$  and  $N_2$ ) was demonstrated.

#### 8.1.2 Molecular Reaction Mechanism

Based on the observation that  $NH_3$  was formed during etching under the applied process conditions, the previously reported reaction mechanisms could be limited to two alternatives. The only difference between these was the formed gallium-oxygen species.

$$GaN + 3 H_2O \rightarrow Ga(OH)_3 + NH_3$$

$$(8.6)$$

$$2 \operatorname{GaN} + 3 \operatorname{H}_2 O \rightarrow \operatorname{Ga}_2 O_3 + 2 \operatorname{NH}_3$$

$$(8.7)$$

Whereas one potential mechanism contained the formation of  $Ga(OH)_3$ , the alternative reaction product was  $Ga_2O_3$ . In both cases, KOH is not consumed during the reaction, but acts as a catalyst. In the first reaction step, nucleophilic attack of hydroxide ions on positively charged Ga is feasible, which generates Ga-OH bonds.  $Ga(OH)_3$  then immediately dissolves in acidic and alkaline solution under formation of  $[Ga(H_2O)_6]^{3+}$ and  $[Ga(OH)_4]^{-}$ , which was reported before [117].

 $Ga_2O_3$ , on the other hand, generally forms out of  $Ga(OH)_3$  by heating under intermediate formation of GaO(OH). Based on the initial Ga-OH bonds developed during etching, further reaction would be required. It was considered that the formation of  $Ga_2O_3$  could be favorable due to release of water. As water is consumed during the reaction and also accomplishes hydration of the high ion concentration, a shortage was something to expect. However, also the dissolution of  $Ga_2O_3$  in strongly alkaline solution leads to the formation of  $[Ga(OH)_4]^-$ . Eventually cleaved water would therefore have to be consumed again. As a consequence, no plausible explanation for an eventual reaction to  $Ga_2O_3$  was found. These considerations led to the molecular etch reaction to consist out of the following consecutive combination. 8.1 Substitution Mechanism under NH<sub>3</sub> Formation

$$GaN + 3 H_2O \rightarrow Ga(OH)_3 + NH_3$$

$$(8.8)$$

$$4 \text{ Ga}(\text{OH})_3 + 6 \text{ H}_2\text{O} \rightarrow [\text{Ga}(\text{H}_2\text{O})_6]^{3+} + 3 [\text{Ga}(\text{OH})_4]^{-}$$
 (8.9)

After the initial hydroxide ion attack on Ga, the negative charge at N is neutralized by reaction with a proton from solution, which explains well the ER peak at 23 wt. % aq. KOH (Equation 8.10). At low KOH concentrations, the availability of OH<sup>-</sup> is low as well. Also the solubility of Ga(OH)<sub>3</sub> is poor in a relatively neutral pH range. At high KOH concentrations, water and especially protons are not available for the actual etch reaction due to solvation of KOH and the generally low H<sup>+</sup> concentration.

In further  $OH^-$  and  $H^+$  catalyzed partial reactions,  $NH_3$  and  $Ga(OH)_3$  are formed and dissolved (Equation 8.11, Equation 8.12). Thereby, step by step, Ga-N bonds are substituted by Ga-OH and H-N bonds. By dissolution of the reaction products, the initial surface condition is recovered on the  $(000\overline{1})$  N-face. The etch process thus runs in cycles, which has been reported before [83, 106, 118].



#### 8 Molecular Etch Mechanism and Directional Anisotropy

At this point, it must be clarified that the determined reaction mechanism is valid for the here applied process conditions. Diffusion limitation had been reported under PEC conditions [85, 92, 93]. As soon as holes are generated e.g., by light irradiation or positive bias voltage, the mechanism changes as well as rate determining step.

In summary, the reaction mechanism occurring during GaN etching in aq. KOH solution without application of light or bias voltage was clarified. Based on the previously reported mechanistic approaches, experiments were conducted, which proved the formation of  $NH_3$ . Combined with the quick dissolution of the formed Ga species  $Ga(OH)_3$ , one feasible molecular reaction mechanism remained. Depending on the process conditions, however, a change in the reaction mechanism is expected. Especially once electron-hole pairs are formed inside the material, their participation should lead to a redox etch mechanism.

## 8.2 Molecular Explanation for Anisotropic Etching

Next to the molecular reaction, the reason for the development of hexagonal pyramids was investigated on the atomic level. Before, was already proven by AFM that the pyramidal side facets represent the  $\{10\overline{11}\}$  crystal planes (section 5.3). A model for the relative resistance of different crystal planes against etching is elaborated and presented below.

#### 8.2.1 Selectivity of N-face over Ga-face Etching

In aq. solution, the GaN surface reacts under dissociative water adsorption [119]. Thereby, protons bond to surface-standing nitrogen, whereas hydroxide bonds to Ga. Prior to etching, the surface states of the Ga-polar and N-polar GaN surface in aq. solution are shown in Figure 8.3. The relative Ga-N, Ga-O, O-H and N-H bond lengths are true to scale with literature values of 1.96 Å, 1.92 Å, 0.98 Å and 1.01 Å [120–126].

In case of Ga-face GaN (Figure 8.3, left), Ga is initially directly open to solution allowing for hydroxide attack. The top Ga layer can thus be easily etched. After removal of the first Ga layer, the surface is, however, terminated by  $NH_2$  groups. These protrude vertically from the surface (Figure 8.4, right). Two hydrogen atoms



Figure 8.3: Schematic crystal lattice of Ga-polar (0001) (left) and N-polar (0001) (right) GaN surface. Hereby, the top face in both figures represents the respective surface. Hydroxide and proton bonding to Ga and N at the surface is shown as it generally occurs in aqueous solution under dissociative water adsorption. Black, blue, red and white spheres represent Ga, N, O and H.

of  $NH_2$  groups provide steric hindrance. Each surface-standing nitrogen atom also has a non-bonding electron pair additionally blocking the approaching of negatively charged  $OH^-$  ions. The combination of both electronic and steric hindrance explains the effective etch stop on Ga-polar GaN.

Compared to that, the N-face GaN surface state is initially covered by N-H groups without the presence of free electron pairs (Figure 8.3, right). The N-H bonds only have a 19° angle relatively to the lateral (000 $\overline{1}$ ) plane. This leads to significantly less hindrance against OH<sup>-</sup> attack compared to the Ga-polar situation after removal of the top Ga layer. Ga is therefore accessible, which is indicated by the green arrows in



Figure 8.4: Schematic removal of single Ga atom layer from Ga-polar (0001) GaN surface by reaction with  $OH^-$ . This results in termination with  $NH_2$  groups protruding with a 90° angle relatively to the lateral (0001) plane effectively blocking further etch progress. The attack of incoming hydroxide ions is complicated due to repulsion between these and  $NH_2$ .

Figure 8.5. Once one GaN layer is removed, the initial surface situation is recovered again. The consequence is steady etching of N-face GaN.

For Ga-polar GaN, dark etching without voltage and above-band gap illumination has been reported to only remove material around crystal errors including TDs [101, 127, 128]. In these positions, the hindrance by  $NH_2$  groups is interrupted. This allows for  $OH^-$  access. Under PEC conditions, a strong attraction between negative hydroxide and the positively biased GaN material exists. The hindrance is thereby overcome so that Ga-polar material can be etched. Hereby, TDs have an opposed effect as under dark conditions. The GaN material directly around TDs remains intact, whereas intact crystal regions are dissolved. Non-radiative recombination of photo-induced electron-hole pairs occurs at a higher rate at TDs due to additional electron transitions. The lower availability of excited electron-holes pairs for the electrochemical PEC etch reaction slows down the ER leading to so-called whisker formation around TDs [129].

The distinction between N-face and Ga-face GaN and the concept of steric and electronic hindrance has been reported before and serves as a basis for the following considerations [62, 83, 106].



Figure 8.5: Schematic removal of single Ga atom layer from N-polar (0001) GaN surface by reaction with OH<sup>-</sup>. This results in termination with NH groups protruding with a 19° angle relatively to the lateral (0001) surface allowing for further etch progress. After the first removed GaN layer, the identical surface state is recovered as before. This is the basis for a constant etch process running in cycles.

#### 8.2.2 Stability of Pyramid Side Facets

The development of pyramids with  $\{10\overline{11}\}\ crystal facets is necessarily a consequence of$  $a higher stability of the side facets compared to the <math>(000\overline{1})\ N$ -face. If that was not the case, pyramids would be etched preferably and the surface would saturate at the  $(000\overline{1})$ plane. In the following, the schematic  $\{10\overline{11}\}\ crystal$  facet is shown on the atomic level (Figure 8.6, left). Hereby, the angled left crystal facet represents the  $\{10\overline{11}\}\ plane$ including protonation of surface-standing nitrogen atoms. Based on the crystal lattice, rows of nitrogen atoms protrude from the  $\{10\overline{11}\}\ surface$  with alternating angles of 79° (first and third row from the top) and 35.5° (second and fourth row from the top) relatively to the  $\{10\overline{11}\}\ facet$ . The situation can thus be understood as an intermediate between N-polar and Ga-polar crystal facets. Thus, a  $\{10\overline{11}\}\ ER$  between the ERs of  $(000\overline{1})\ and\ (0001)\ facets\ could\ be\ expected.$  This agrees with the experimental results.

Some etch experiments showed the temporary formation of the  $\{1\overline{2}1\overline{4}\}$  crystal facet on top of  $\{10\overline{11}\}$  pyramids. The identity of the  $\{1\overline{2}1\overline{4}\}$  plane was determined by AFM measurement resulting in a  $38.2^{\circ} \pm 0.7^{\circ}$  angle of the pyramid side facet relatively to the  $(000\overline{1})$  base plane (Figure 8.7, lect, green line, mean  $\pm$  SDM, n = 3). The theoretical angle of the  $\{1\overline{2}1\overline{4}\}$  facet has a value of  $39.2^{\circ}$ . For comparison, the underlying final



Figure 8.6: Schematic surface termination of  $\{10\overline{11}\}$  pyramid side facets with NH<sub>2</sub> group termination (left). NH<sub>2</sub> groups protrude at alternating angles of 79° and 35.5° relatively to the  $\{10\overline{11}\}$  pyramid facet. The steric and electronic hindrance leads to a more hindered OH<sup>-</sup> attack compared to the lateral (000 $\overline{1}$ ) plane. Schematic surface termination of  $\{1\overline{2}1\overline{4}\}$  pyramid side facets with NH<sub>2</sub> group termination (right). The surface consists out of a terrace structure with local (000 $\overline{1}$ ) plateaus in between  $\{10\overline{11}\}$ slopes. This situation leads to preferred etching of the  $\{1\overline{2}1\overline{4}\}$  planes over  $\{10\overline{11}\}$  facets. The theoretical consideration is in agreement with the experimental results.

#### 8 Molecular Etch Mechanism and Directional Anisotropy

 $\{10\overline{11}\}\$  facet is represented by the red line in Figure 8.7, left. The schematic  $\{1\overline{2}1\overline{4}\}\$  facet is shown as the angled left facet in Figure 8.6, right. A stepped structure is visible in the schematic. The sequence alternates between the situations discussed for  $(000\overline{1})$  and  $\{10\overline{11}\}\$  facet etching. The ER must therefore have a value in between both the latter crystal planes. This explains the intermediate formation during the transition from a polished  $(000\overline{1})$  to the final  $\{10\overline{11}\}\$  terminated surface.

In conclusion, the literature-known concept of hydroxide repulsion by protruding NHand NH<sub>2</sub>-groups was further elaborated. Thereby, the ER of the regular  $\{10\overline{11}\}$  pyramid side facets could be explained on the atomic level. Also, the temporary formation of  $\{1\overline{2}1\overline{4}\}$  pyramids could be attributed to an ER in between the lateral  $(000\overline{1})$  facet and the more stable  $\{10\overline{11}\}$  pyramid side facets. The smaller the angle between pyramid facet and  $(000\overline{1})$  plane becomes, the higher is the relative percentage of  $(000\overline{1})$ coverage of the terrace structure. This results in a higher ER. The maximum ER is reached at the  $(000\overline{1})$  plane with an obvious angle of 0°.



Figure 8.7: 3D AFM image of GaN sample A after etching in 30 wt. % aq. KOH solution at 80 °C for 6 min (left). The lateral size of the measurement field equals  $2 \cdot 2 \,\mu m^2$ . The green and red lines mark  $\{1\overline{2}1\overline{4}\}$  and  $\{10\overline{11}\}$  planes with measured angles of  $38.2^{\circ} \pm 0.7^{\circ}$  and  $62.9^{\circ} \pm 1.0^{\circ}$  (mean  $\pm$  SDM, n = 3) relatively to the (000 $\overline{1}$ ) base plane. Schematic OH<sup>-</sup> attack on  $\{1\overline{1}00\}$  GaN surface (right). NH and NH<sub>2</sub> groups protrude with angles of 0° and 81° from the  $\{1\overline{1}00\}$  causing repulsion of incoming OH<sup>-</sup> ions. This leads to a low ER, especially when compared to the lateral (000 $\overline{1}$ ) crystal facet.

#### 8.2.3 Stability of Non-Polar Crystal Facets

The non-polar  $\{1\overline{1}00\}$  crystal facet shows protruding NH<sub>2</sub> groups with a 81° relative angle to the  $\{1\overline{1}00\}$  plane on the atomic level (Figure 8.7, right). In between these, NHgroups cause further hindrance with  $0^{\circ}$  relative angle to the  $\{1\overline{1}00\}$  facet. The expected low ER was confirmed by SEM analysis of a grinded bulk GaN substrate wafer before and after etching in 30 wt. % aq. KOH at 80 °C for 120 min (Figure 8.8). The long etch time was chosen to reveal the most stable crystal facets. Before etching, a large size variation of grinded GaN particles was observed (Figure 8.8, top). The particles showed multiple and undirected crystal orientations. During etching, all small GaN particles were dissolved. With an expected ER of  $\sim 350 \text{ nm min}^{-1}$ , particles with > 50 µmdiameter were not dissolved entirely. The remaining large particles showed smooth crystal facets with terrace structures (Figure 8.8, bottom). At a higher magnification,  $\{10\overline{11}\}$  pyramids were found on the bottom end of a single particle (Figure 8.9, top). The side planes of these directly terminated at non-polar  $\{1\overline{1}00\}$  facets. On the other end of the latter facets, flat (0001) plateaus were formed with sharp edges. Etch progress occurred exclusively in terrace-patterns. The sharp transition between (0001) plateaus (dark) and  $\{1\overline{1}00\}$  facets (bright) is visible at a steeper angle in Figure 8.9, top.



Figure 8.8: SEM images of grinded bulk GaN substrate wafer pieces before (top) and after etching in 30 wt. % aq. KOH solution for 120 min at 80 °C (bottom). Small particles were dissolved during etching, whereas large particles developed a terrace structure with smooth crystal facets.

#### 8 Molecular Etch Mechanism and Directional Anisotropy

Once a crystal facet besides the three most stable ones (i.e., (0001),  $\{1\overline{1}00\}$  and  $\{10\overline{11}\}$ ) is formed locally, etching of this occurs at a higher ER. This leads to selective material removal perpendicular to the formed facet. This lateral etching further on causes a progressing terrace. Based on these observations, the susceptibility towards etching of the three discussed crystal facets could be determined as  $\{1\overline{1}00\} > \{10\overline{11}\} > (0001)$ .

The non-polar  $\{1\overline{1}00\}$  facet must thereby be etched more quickly than the  $\{10\overline{11}\}$  plane. Otherwise, the  $\{1\overline{1}00\}$  plane would be formed during regular etching from the N-face eventually resulting in vertical GaN pillars with pyramid tips. As this was not observed and only  $\{10\overline{11}\}$  pyramids appeared on the N-polar surface after etching, the respective crystal facets must have higher stability against etching. The relative ERs of  $\{1\overline{1}00\}$  and  $\{10\overline{11}\}$  facets agrees with the calculated angles of NH- and NH<sub>2</sub>-groups relatively to the crystal facets.

In summary, also the ER of non-polar  $\{1\overline{1}00\}$  crystal facets could be explained by application of the hydroxide repulsion model. Long-term etching of bulk GaN combined with subsequent SEM analysis was applied to prove an increasing relative ER order of  $(0001) < \{10\overline{11}\} < \{1\overline{1}00\}$  crystal facets.



8.2 Molecular Explanation for Anisotropic Etching

**Figure 8.9:** High magnification SEM images of grinded bulk GaN substrate wafer pieces after etching in 30 wt. % aq. KOH solution for 120 min at 80 °C. He-xagonal crystal facets were formed, whereby smooth sections were ordered in terrace-shape.

### 8.2.4 Pyramid Size Increase during Proceeding Etching

Once the initial N-polar  $(000\overline{1})$  surface had developed into a  $\{10\overline{11}\}$  pyramid pattern, one would expect simultaneous etching of all crystal planes based on the constant ER of identical crystal planes (Figure 5.6, left). However, all experiments showed that pyramids evolved larger with an increasing etch time. Figure 8.10 shows the schematic situation on an atomically sharp  $\{10\overline{11}\}$  pyramid tip. Even under the assumption, that the pyramid tip is atomically sharp, it still represents a microscopic  $(000\overline{1})$  plateau on its tip. As a consequence, etching of the tip is preferred over the pyramid side walls. During etching, the GaN surface has a tendency to decrease the number of pyramid tips relatively to the  $\{10\overline{11}\}$  area. By simultaneous etching of the tip and the  $(000\overline{1})$ base plane at the pyramid bottom, pyramids evolve larger and thereby reach increasing stability against etch removal by maximizing the  $\{10\overline{11}\}$  surface relatively to the total GaN surface.

On the other hand, the development of large pyramids includes the long-term stability of their tips. As stated above, the pyramid tips are etched preferably and thus are eroded at one point. This was observed in foregoing experiments, as no pyramid tip remained stable for more than 2 min etch time. Both tendencies of the surface to increase the area of cohesive pyramid facets on the one hand and to dissolve the pyramid tips preferentially on the other hand might combine to a constant equilibrium of pyramid formation and erosion. During etching, this supposedly results in a steady increase in average pyramid size. If and to which extent also other influences including electronic effects impact the microscopic development of pyramids could not be determined at this point.

# 8.2.5 Hydroxide Attack as Rate Determining Step in Etch Reaction

Not only could the atom geometry explain the relative stability of individual crystal facets and boundaries, but also the rate determining step in the reaction mechanism (compare section 8.1). The initial hydroxide formation consists out of  $OH^-$  attack on Ga and  $NH_3$  formation.



Figure 8.10: Schematic tip of GaN pyramid with  $\{10\overline{11}\}$  side facets. The atomically sharp tip shows the identical situation which is present at the  $(000\overline{1})$  plane. This leads to preferred etching of pyramid tips compared to the side facets. The consequence is a tendency of the surface towards large pyramids to increase the  $\{10\overline{11}\}$ : $(000\overline{1})$  ratio.

Based on the considerations, the  $OH^-$  attack must be the rate determining step. If NH<sub>3</sub> formation was the critical step, the etch selectivity would have to be reversed. Especially on the (0001) Ga-face, nitrogen is presented towards the KOH solution with a 90° angle relatively to the (0001) base plane. Nitrogen thus has optimum accessibility towards the KOH solution. If NH<sub>3</sub> attack was the rate determining step, the high accessibility would cause a quicker reaction than in case of N-face material. This is obviously not the case as the ER of Ga-polar GaN is very low compared to the N-polar surface.

In conclusion, several empirical observations could be explained by extending the literature-known model of hydroxide repulsion by NH- and  $NH_2$  groups. By transferring the model to semi-polar and non-polar crystal facets as well as pyramid tips, the relative ERs were clarified. Also, the model explained the steady increase in average pyramid size as well as that hydroxide attack on Ga is the rate-determining step of the reaction mechanism.

# 8.3 Electronic Influence on Etch Rate

Considering the reaction mechanism and the root cause for anisotropic etching, an electronic influence on the ER was not obvious up to this point. Hydroxide ions are attracted by the positively charged Ga atoms. Subsequently, Ga-OH bond formation is the first step of the reaction mechanism. The rate of the first reaction step is influenced by the Ga charge, which again is influenced by the charge of the entire GaN layer.

#### 8.3.1 Charge Effect of Entire GaN Layer

As soon as GaN is negatively polarized, the global negative charge repulses incoming  $OH^-$  and thus leads to a slowed-down ER. This situation was observed during p-GaN etching before, where it appeared as dopant selective etching [130]. Due to downward surface band bending in case of p-GaN, electrons that are excited into the conduction band  $E_{CB}$  accumulate at the solution-GaN interface (Figure 8.11, left). This causes negative polarization of the surface relatively to the positively polarized bulk material and a lower ER due to  $OH^-$  repulsion. As soon as an electron is excited into the CB, the lower  $E_{CB}$  at the GaN-solution interface compared to the bulk material leads to electron drifting towards the interface. The remaining hole at the interface drifts into the bulk crystal, which in the first place does not seem intuitive. However, the hole conduction mechanism is equivalent to the reverse electron flow. Also in the VB, electrons in higher orbitals take up the space of a formed hole due to the lower energy of the free orbital. Simultaneously, the hole travels away from the interface in opposite direction.

In n-GaN, upward band bending accumulates holes at the surface. This corresponds to the inverse effect. The positive polarization of the surface provides a higher rate of  $OH^-$  attack and thus explains a functioning etch progress. It was observed during the course of this work, that N-face p-GaN is still etched if it is a part of an epitaxial layer stack (e.g., **A**). A higher ER by positive polarization of the entire material can be explained by these considerations in the same way as a decreased ER in case of negative polarization.



Figure 8.11: Schematic surface band bending of p-GaN (left) and n-GaN (right) at the GaN-solution interface. Downward band bending in case of p-GaN causes accumulation of electrons at the surface combined with a negative polarization. The opposite situation in n-GaN leads to a positive polarization by the drifting of positively charged holes towards the GaNsolution interface [102, 130, 131]. Etching of n-GaN thus functions due to the attraction of negatively charged hydroxide ions. On the other hand, p-GaN depends on a positive bias voltage and/or above-band gap illumination to be etched.

#### 8.3.2 Local Charge Distribution

Also on a small and local scale, ER differences were observed. Although LLO caused the main part of local etch inhomogeneity on a wafer base, also the presence of noble metals on the surface was found to influence the local ER. Au and Pt grids with a thickness of 100 nm were deposited directly on top of BOE pretreated wafers **A**. AFM and SEM analysis showed that the ER was lower near the metal edges (Figure 8.12). *The average GaN pyramid size was decreased within 3 µm distance from the noble metal* grid edges after etching in 30 wt. % aq. KOH at 80 °C for 6 min. AFM analysis proved the higher z-niveau in these regions. No difference in local etch progress was thereby found between samples with Au or Pt grids. Diffusion did not cause the lower ER. This was investigated by repetition of the identical experiment with a 300 nm thick SiN<sub>x</sub> grid instead of the noble metals. In this experiment, the average pyramid size was homogeneous in the entire etched area without a systematic decrease towards the SiN<sub>x</sub> edges (Figure 8.13).

#### 8 Molecular Etch Mechanism and Directional Anisotropy

A change in the conductivity of the GaN-metal composite possibly caused a lower positive polarization of the surface and thus a slower etch reaction. Over the course of this work, it was shown that neither the local dislocation distribution nor the individual positions of LLO surface roughness features was accountable for the exact position of pyramid tips. Eventually minor differences in the local conductivity and potential of the GaN layer cause the individual stability of tips and valleys, which could not be definitely determined. Significant influence on the local GaN ER by manipulation of the electronic situation in GaN will be presented and discussed in chapter 9.



**Figure 8.12:** SEM image of GaN sample **A** with physical vapor deposited Au grid (100 nm thickness) after etching in 30 wt. % aq. KOH for 6 min at 80 °C (left). AFM image of the identical sample with scan size  $20 \cdot 6.7 \,\mu\text{m}^2$  (right). Close to the Au edge, the ER of GaN was decreased compared to the remaining GaN surface. This is visible by means of the smaller pyramids and higher z-niveau of the GaN surface in this surface section.



Figure 8.13: SEM images of GaN sample A with CVD deposited  $SiN_x$  grid (300 nm thickness) after etching in 30 wt. % aq. KOH for 6 min at 80 °C. An overview image (left) is shown as well as higher magnification images at angles of 45° (center) and 90° angles (right). Whereas the proximity to deposited gold decreased the local GaN ER, the same experiment with  $SiN_x$  instead of Au or Pt had no influence on the local GaN ER. The average pyramid size and distribution was homogeneous across the entire GaN surface.

# 9 Etch Rate Manipulation by Electron Irradiation

Several studies exist describing the interaction between GaN and an irradiated electron beam [132–135]. Especially high-energy electron irradiation on GaN (0.45 MeV - 2.5 MeV) led to the creation of point defects (i.e., N vacancy, N interstitial, Ga vacancy, Ga interstitial). Whereas 0.45 MeV irradiation energy disturbed the N-sublattice, 2 MeV electron energy led to implantation of Ga-sublattice defects. The annealing temperature necessary to degrade the induced defects increased with irradiation energy. These defects were characterized by PL measurement due to their impact on the electronic characteristics of the material [136]. The influence on the electronic characteristics of the material also implied an effect on the wet-chemical ER.

# 9.1 Surface Structuring with Point-, Line- and Circularly-Shaped Patterns

At a significantly lower energy than in the previously reported studies (i.e., 8 keV), electron irradiation was applied on GaN samples **A** after BOE pretreatment. A  $5 \cdot 5$  point grid was irradiated with an irradiation time of 5 s per pixel and a beam focus diameter of 20 nm. Afterwards, etching in 30 wt. % aq. KOH solution was performed for 6 min at 80 °C (Figure 9.1, top left). The initial irradiation positions are indicated by red dots. During etching, less material removal was reached in irradiated positions. This led to the formation of pyramids with defined tips. The concept of structuring the GaN surface without previous application of a photo lacquer mask has not been reported earlier and presents a very promising tool for future chip processing.

#### 9 Etch Rate Manipulation by Electron Irradiation



Figure 9.1: SEM images of 8 keV electron beam irradiated GaN samples A after 6 min etching in 30 wt. % aq. KOH solution at 80 °C. Irradiation was conducted with 20 nm focus width as point grid (top left), linear (top center) with 15 µm (top right) and 45 µm (bottom left) length divided by 100 pixels, circular (bottom middle) and individual smiley shape (bottom right). Irradiation time was set to  $1 \text{ s pixel}^{-1}$  for point grid and 100 ms pixel<sup>-1</sup> for all other shapes. Irradiated surface sections were etched at a significantly lower ER. This led to successful surface structuring by the combination of electron irradiation and subsequent etching.

Also linear shapes could be realized with an even lower irradiation time of 100 ms per pixel (Figure 9.1, top middle). Lines with 100 pixels were irradiated with a total length of 15 nm (Figure 9.1, top right) and 45 nm (Figure 9.1, bottom left). The individual pixels were visible as pyramid tips after etching. Also circular and individual shapes could be achieved (Figure 9.1, bottom middle and right). Possible applications include the individual labeling of LED chips with an identification number. Also, concentric circular patterns could be applied to function as a Fresnel lens [137]. Thereby, the light emission could be designed directly on the chip surface rather than package design. Another interesting application is the creation of a regular or quasi-regular pyramid grid. This technique can combine the benefits of wet-chemical roughening, i.e., low surface damage, low complexity and low cost, with the predictability of dry-chemical roughening.

# 9.2 Variation of Electron Irradiation Parameters

In terms of electron irradiation parameters, the influence of irradiation time, beam focus and acceleration voltage was investigated. First, at an energy of 8 keV, doses of 10 ms, 100 ms, 1 s, 2 s, 3 s, 4 s, 5 s and 10 s were irradiated on a GaN sample **A** with 20 nm focus width. After etching in 30 wt. % aq. KOH solution, pyramids formed after 10 ms irradiation time could not be visually distinguished from the surrounding surface (Figure 9.2). Thus, the etch selectivity between irradiated and non-irradiated GaN was low. Between 100 ms and 10 s, however, the developed pyramid pattern could easily be identified on the surface. More distinct irradiation features (e.g., linear, circular) might have been distinguishable from the surrounding surface also at lower irradiation doses than 100 ms pixel<sup>-1</sup> due to the strong distinction from the random pyramidal surface. For productive application, the lowest possible irradiation dose should be selected to minimize material alteration and process time. In the following experiments, 100 ms pixel<sup>-1</sup> were used.

In terms of focus width, 20 nm was the smallest possible diameter that could be reached with the used experimental setup. As soon as the electron beam was widened by manual defocussing, no pattern formation could be observed anymore after etching. *Thus, the local electron intake per surface area was lowered to a point where no etch selectivity was found.* This correlated well to the small selectivity found at a low irradiation time of 10 ms.

The acceleration voltage was varied between 5 kV and 12 kV. After irradiation of 15 µm lines with 100 pixels and etching in 30 wt. % aq. KOH, the resulting patterns were visually identical (Figure 9.3). The investigated range of kinetic energy of electrons did not lead to a visible change in etch selectivity.

In conclusion, the etch selectivity between irradiated and non-irradiated GaN regions increased with irradiation dose. The acceleration voltage showed no impact when varied between 5 keV and 8 keV.



Figure 9.2: SEM images of 8 keV electron beam irradiated GaN samples A after 6 min etching in 30 wt. % aq. KOH solution at 80 °C. Irradiation was conducted with 20 nm focus width as point grid. Irradiation time was varied between 0.1 s and 10 s as indicated in the single images. The scale bar refers to all images. After a minimum irradiation time of 100 ms per pixel, the induced pyramid tips were distinguishable from the surrounding pyramid pattern. The etch selectivity between irradiated and non-irradiated surface sections increased with electron dose.



Figure 9.3: SEM images of electron beam irradiated GaN samples A after 6 min etching in 30 wt. % aq. KOH solution at 80 °C. Irradiation was conducted with 20 nm focus width a linear arrangement of 100 pixels and 100 ms pixel<sup>-1</sup> irradiation time. The acceleration voltage was varied between 5 keV and 12 keV. No influence on the appearance of the line patterns was observed. The scale bar refers to all images.

# 9.3 Variation of Etch Time

Next to the irradiation process, also the etch time in KOH solution was varied. Samples **A** were irradiated with 15 µm lines with 100 pixels at 8 keV and 20 nm focus width. Etching was performed in 30 wt. % aq. KOH at 80 °C. The etch time was varied between 1 min and 6 min. Over the entire 6 min etch time, the linear patterns were visible (Figure 9.4). Whereas the line shapes were not significantly etched, the surrounding surface showed the expected plateau after 1 min etch time and an increasing average pyramid size from 2 min to 6 min (compare Figure 5.3 and Figure 5.4). In irradiated areas, the SiN<sub>x</sub> plateau was crossed after 4 min etch time. After 5 min and 6 min etching, sharp pyramid tips were visible in the positions of every pixel. Thus, also the irradiated material was etched, although at a lower rate.



Figure 9.4: SEM images of 8 keV electron beam irradiated GaN samples after 1 - 6 min etching in 30 wt. % aq. KOH solution at 80 °C. Irradiation was conducted with 20 nm focus width, linear shape and 100 ms pixel<sup>-1</sup> irradiation time. The scale bar refers to all images. The linear patterns remained intact over 6 min etching. Thereby, also on top of the lines, material removal was observed. As a consequence, the local ER in irradiated positions was decreased but not entirely eliminated.
### 9.4 Mechanistic Influence of Electron Irradiation

Two basic hypotheses were formed explaining the decreased ER in irradiated crystal sections. First, carbon deposition during electron irradiation was considered. While functioning as a temporary mask, a steric hindrance could complicate hydroxide access to Ga. Secondly, the presence of point defect complexes (e.g., trapped electrons, interstitial and vacancy defects in Ga and N sublattice) generally causes a change in the electronic properties of the crystal [138]. Irradiated electrons could activate electronic band transitions at such defects and thus influence the ER. Also, an implanted negative charge could complicate the rate-determining OH<sup>-</sup> attack. Both steric and electronic hypotheses were investigated and are discussed in the following.

#### 9.4.1 Detection of Carbon Impurities before and after Etching

After etching, hazy deposits were regularly observed under SEM analysis (Figure 9.5, left). With in-lens SEM observation, these residues appeared as dark spots showing increaed charging compared to GaN (Figure 9.5, middle). EDX analysis of the deposits compared to the surrounding surface showed carbon and oxygen presence in the irradiated areas (Figure A.8). This hinted towards carbon deposition in the first place. In a second EDX experimental run, these experiments could not be confirmed (Figures A.9 and A.10). Therefore, AES was performed (Figures A.11, A.12, A.13, A.14, A.15 and A.16). In the irradiated area, the carbon concentration was particularly high after etching. *Before etching, however, no carbon presence could be detected*. Instead, a white contrast was observed under SEM in irradiated positions, which decayed within minutes (Figure 9.5, right). Therefore, the organic material observed after etching had to be deposited during or after the etch process. Moreover, also the material in the irradiated position was eroded at a slower rate. The presence of a conventional mask would not have led to a slow etch attack. *Carbon deposition by electron beam irradiation could be excluded at this point*.

#### 9 Etch Rate Manipulation by Electron Irradiation



Figure 9.5: 45° SEM image of two irradiated lines on GaN sample A (8 keV, 100 ms pixel<sup>-1</sup>, 20 nm beam diameter) after etching for 6 min etching in 30 wt. % aq. KOH solution at 80 °C (left). Top-view in-lens SEM image of GaN sample processed under identical conditions (middle). Dark hazy residues were present on the irradiated features as well as on top of a few surrounding pyramid tips. This finding initially indicated that a masking effect by carbon could be the root cause for the decreased etch susceptibility. This was, however, proven wrong later on. SEM image of GaN surface A directly after irradiation of point grid (8 keV, 5 s pixel<sup>-1</sup>, 20 nm beam diameter) showing white contrasts in irradiated areas (right). This indicated an electronic effect changing the conductivity or charge of the material.

#### 9.4.2 Activation of Point Defects

The creation of intrinsic point defects in GaN has activation energy values of at least 0.7 MeV [132]. The energy of irradiated electrons used during the course of this work was much lower. Therefore, the creation of new defects was not considered as possible. However, the intrinsic point defect density in epitaxial GaN is usually in a range of  $10^{18}$  compared to  $4.5 \cdot 10^{22}$  atoms cm<sup>-3</sup> [139, 140]. Directly after the epitaxial growth, passivation of such defects by hydrogen or other precursor decomposition products could be the case. Thus, these defects would not be electronically active. *Possibly, the energy uptake caused by the electron beam activates these defect centers leading to the insertion of additional electronic states in the material*. Thereby, new radiative and non-radiative transitions could be created effectively competing with the donor-bound exciton (E<sub>g</sub>). This change in the electronic properties of the crystal might cause a lower rate of the rate-determining hydroxide attack.

To investigate this mechanistic hypothesis, time-resolved CL measurement was conducted. The 8 keV electron beam used for CL analysis was directed at a single GaN surface spot. In 10s intervals, CL spectra were recorded for a total time of 70s. Thereby, the band gap emission was monitored (Figure 9.6). The longer the sample was exposed to electron irradiation, the lower was the intensity of the band gap emission. The band gap energy itself remained unchanged. The experiment showed the generation of competing electronic transitions.

Buyanova and his group [136] observed complete quenching of the donor-bound exciton caused by 2.5 MeV electron irradiation with high doses  $> 1 \cdot 10^{18} \text{ cm}^{-2}$ . Compared to these results, the effect during this work was smaller only partially quenching the donor-bound exciton emission.

In conclusion, the mechanistic hypothesis of carbon deposition on top of GaN effectively causing the lower ER could be excluded. By time-resolved CL measurement, a decrease in band gap emission over irradiation time was observed. Presumably, by electron irradiation, passivated intrinsic crystal defects were activated.



Figure 9.6: CL spectra of  $E_g$  band gap GaN emission recorded during 70s electron beam irradiation in 10s intervals (8 keV, 20 nm beam diameter). With increasing irradiation time, the  $E_g$  band gap emission decreased. This indicated the activation of additional electron transitions and thus a less efficient  $E_g$  emission.

### 9.5 Application on Other Materials and Processes

GaN samples  $\mathbf{A}$ , which were used during the initial electron beam irradiation experiments, had no MQW in the epitaxy layer stack. Under identical irradiation and etch conditions as above, also with MQW electron beam structuring was investigated and proven functional.

Also etching of GaN **A** in  $H_3PO_4$  was influenced by electron irradiation. By 5 min etching in 85 wt. %  $H_3PO_4$  at 150 °C, almost the entire GaN layer stack was removed, which revealed the lot metal. Only single free-standing pyramids were left on the surface. The irradiated point grid, however, was present and easily distinguishable (Figure 9.7).



Figure 9.7: SEM images of 8 keV electron beam irradiated GaN samples after 5 min etching in 85 wt. % aq.  $H_3PO_4$  solution at 150 °C. Irradiation was conducted with 20 nm focus width as  $5 \cdot 5$  point grid and 100 ms pixel<sup>-1</sup> irradiation time. Electron irradiation also yielded a lower relative ER during etching in aq.  $H_3PO_4$  solution.

# **10** Conclusion

The etch process of GaN in aq. KOH solution was characterized during the course of this work. Utilizing ICP-OES, a novel method was developed to determine the etch kinetics of GaN with unprecedented precision. Thereby, the total amount of dissolved Ga in KOH solution was measured. Matrix adaption of sample and ICP-OES standard solutions achieved a measurement precision of 0.8% deviation between measurement result and the actual dissolved Ga mass. The reproducibility of the method was 1% relative SDM and therefore superior to the smallest reached material variation of 3% without foregoing polishing of the samples. By ICP-OES, two major disadvantages of other reported methods for ER determination (i.e., weighing and height profilometry) could be circumvented.

The first advantage compared to previously reported methods was that samples could be drawn without interruption of the etch process. Thereby, surface oxidation did not take place in between etch steps, which eventually would have caused overestimation due to better solubility of the respective Ga-oxygen species compared to GaN. The depth-dependent ER could thus be resolved for each individual epitaxial GaN layer of complex layer stacks. Secondly, the rough surface amplitude due to pyramid formation caused significant measurement error during height profilometry, which has been reported before. The formed pyramids are many times larger than the usual etch removal per minute. Depending on the exact profilometry measurement position at the bottom or the top of a pyramid, significant error is generated. In contrasts to that, a precise average etch depth could be determined by ICP-OES analysis regardless of surface roughness.

Epitaxial growth conditions have been reported before to be the major influence on the GaN ER. To gain overall understanding of this correlation, the etch kinetics of several different epitaxial layer stacks were analyzed by ICP-OES. The most substrate-near 2D GaN, which was revealed by LLO, was etched at a high ER. At the  $SiN_x$  layer,

#### 10 Conclusion

which usually was located after 300 nm 2D GaN for effective reduction of TD density, temporary saturation of the ER occurred. The saturation was also visible under SEM by formation of a flat plateau. During subsequent etching of 3D GaN, which was grown under different conditions, a constant average ER of  $338 \pm 30$  nm min<sup>-1</sup> was observed in 30 wt. % aq. KOH at 80 °C. From this point on, the whole GaN surface was covered with pyramids, so that both the total surface area as well as the revealed species of  $\{10\overline{11}\}$  crystal facets remained unchanged. This was found to be the basis of a constant ER. During etching, the average pyramid size increased constantly. Individual pyramid tips remained stable for at most 2 min and then broke down to develop smaller pyramids again. Repeated SEM analysis of the identical GaN surface section over several minutes of etching was applied to gain this data. Relocation of the exact spot during SEM analysis was achieved by deposition of a KOH-stable SiN<sub>x</sub> mask. Etching occurred as a constant equilibrium of pyramid formation and breakdown, which was in agreement with foregoing literature.

The pyramid side facets were characterized by AFM, which resulted in an angle of  $61.5 \pm 0.6^{\circ}$  relatively to the lateral (0001) plane. The side facets were identified as  $\{10\overline{11}\}$  crystal planes, which have a calculated theoretical angle of 62.1°. Discordant foregoing literature reports of varying crystal facets could be clarified in this way. To investigate the mechanism of plateau formation at the SiN<sub>x</sub> layer, the position of the latter was varied within the epitaxial stack. After increasing the preliminary 2D GaN thickness to 1000 nm, the plateau in the etch kinetics disappeared. The reason for that was found to be the large z-amplitude of the pyramidal surface, which effectively decreased the percentage of the SiN<sub>x</sub> plateau on the surface relatively to 2D and subsequent 3D GaN pyramids. As a consequence, the slowed down ER was smeared out over several hundred nm of average etch removal.

By  $Al_{0.11}Ga_{0.89}N$  growth directly on top of  $SiN_x$ , the 3D growth direction of subsequently deposited GaN could be circumvented. Still, plateau formation in the etch kinetics occurred. The etch behavior of the 2D GaN layer after the  $Al_{0.11}Ga_{0.89}N/SiN_x$ interface was identical to an experiment without  $SiN_x/Al_{0.11}Ga_{0.89}N$  however. Insertion of the latter layer stack can thus be applied to create an effective etch stop without changing the etch behavior afterwards. For productive application, the temperature dependency of the plateau formation selectivity comes into play. Whereas at 80 °C the  $SiN_x$  plateau was crossed within 1.5 min, etching at RT remained at the plateau for 60 min. At RT, material variation can thus be outsmarted by a selective etch stop. It was found by CLM that under the applied dark and electro-less etch conditions, no correlation existed between pyramid position and individual TDs. On the other hand, correlation was observed between LLO damage and TD density. Supposedly, laser light absorption occurred preferentially in regions with high TD density. This, however, could not be fully confirmed due to a limited availability of data and must be topic in subsequent studies. LLO damage was indeed found to be the main impact on etch non-uniformity across the wafer surface. However, on a microscopic scale no direct correlation between LLO caused surface features and pyramid tip positions was observed.

Two pretreatment strategies were investigated for effective removal of LLO surface roughness. Wet-chemical pretreatment in 30 wt. % aq. KOH at RT further increased non-uniformity compared to the non-pretreated material. Due to the increased materialdependent etch selectivity at RT, the SiN<sub>x</sub> plateau was crossed in some sections of the surface, whereas other sections still had SiN<sub>x</sub> and 2D GaN pyramids in place. During subsequent etching of the sample at elevated temperature, the initial ER variation, which had already been revealed by RT pretreatment, was multiplied.

Mechanical polishing, however, was successfully applied to achieve homogeneous etching over the entire wafer surface. The ER was increased by 500 % by polishing, which could be attributed to a drastic increase in the ratio between  $(000\overline{1})$  and  $\{10\overline{11}\}$  crystal facets. The polished surface exclusively consisted out of the  $(000\overline{1})$  crystal plane. In contrast, the LLO surface roughness resulted in a quick saturation of the surface with pyramids already after 1 min etching. Two processes for productive application of mechanical polishing were proposed, effectively decreasing the WLI determined WIWnon-uniformity from  $7\pm 2\%$  to  $5\pm 1\%$  by creation of a shiny and uniform surface prior to roughening. For the measurement of the WIW non-uniformity, a 51-point WLI method was developed analyzing the roughness homogeneity of an entire 6 inch wafer within 10 min.

For the investigation of process-dependent influences on the ER, a polished 3 µm bulk GaN layer **C** was presented as the sample material of choice. Thereby, the learnings from previous experiments was applied. The high ER reproducibility achieved by polishing and the uniform etch behavior of a homogeneous GaN layer were utilized to visualize even small changes in process control. Variation of the KOH concentration achieved the highest ER at 23 wt. % aq. KOH with an ER of  $318 \pm 15 \text{ nm min}^{-1}$  at 60 °C.

#### 10 Conclusion

The ER decrease towards lower and higher KOH concentrations had been reported in literature before. The exact plateau position could be determined during the course of this work for the first time.

Temperature had an exponential influence on the ER. At RT, an ER of  $12 \pm 1$  nm min<sup>-1</sup> was measured, whereas the ER at 80 °C was  $868 \pm 35$  nm min<sup>-1</sup>. The activation energy  $E_a$  was determined to be  $0.67 \pm 0.04$  eV, which is in the range of kinetically controlled reactions. This corresponded well to the observation that stirring had no influence on the resulting ER. Under the applied process conditions, solution agitation had no effect on the ER.

After analysis of material- and process-dependent influences on the ER, the molecular etch reaction and anisotropy was investigated. The reaction products during GaN etching were identified as  $Ga(OH)_3$  and  $NH_3$  in three separate experimental approaches (i.e., missing bubble formation, pH change in the gas phase over the KOH solution and Berthelot reaction). The reaction mechanism was clarified to be a formal substitution. Both reaction products are quickly dissolved in aq. solution. During etching of N-face GaN, the process runs in cycles, whereby the initial surface condition is recovered after dissolution of a single GaN atomic layer. During the reaction, water is consumed, whereas KOH only acts as a catalyst, which had been reported before.

For the explanation of anisotropic etching, the literature-known concept of hydroxide repulsion was further elaborated.  $OH^-$  attack was confirmed to be the rate determining reaction step. The difference in between the ERs of  $(000\overline{1})$ , (0001),  $\{10\overline{11}\}$ ,  $\{1\overline{1}00\}$  and  $\{1\overline{2}1\overline{4}\}$  crystal facets could be explained by the angle of protruding NH- and NH<sub>2</sub>-groups relatively to the respective crystal facet. In general, the smaller the angle between a pyramid facet and the  $(000\overline{1})$  plane is, the faster occurs the etching of the facet. This was explained by the repulsion of approaching  $OH^-$  ions by the negatively polarized NH- and NH<sub>2</sub>-groups. A model for the constantly increasing average pyramid size during etching was presented for the first time. Pyramid tips have a systematically lower resistance against etching compared to the pyramid side facets. Thereby, a constant equilibrium of pyramid tip breakdown and simultaneous development of large and continuous  $\{10\overline{11}\}$  facets takes place.

Regarding the electronic influence on the GaN ER, it was found that the presence of noble metals directly on the GaN surface decreased the ER of adjacent GaN. Compared to that, the insulator  $SiN_x$  had no influence. Significant electronic influence could be

achieved by electron irradiation prior to etching. This concept was observed for the first time during this work and will be patented by the time this thesis is published. Successful structuring with point-, line-, circular and individual shapes was achieved due to a decreased ER of irradiated GaN surface sections. Structuring of the GaN surface was realized without a foregoing lithography step. The selectivity between nonirradiated and irradiated GaN spots increased with electron dose, which was confirmed by defocusing and a change of the dwell time. No influence on the selectivity was found during variation of the acceleration voltage between 5 kV and 12 kV. The decreased ER in irradiated GaN surface sections was not caused by surface masking, which had been assumed in the first place. Also, the applied electron energy was too low for the creation of additional intrinsic crystal defects. By CL, the band gap emission was determined over 70s in 10s time intervals. A steady decrease in emission was found, which showed the creation of additional electron band transitions. In the proposed mechanism, passivated intrinsic crystal defects were activated by the electron beam energy. The changed electronic properties of the material complicated the hydroxide attack on Ga and thus decreased the local ER.

By characterization of the GaN etch reaction, deep insights into the material- and process dependent influences as well as the mechanistic and anisotropic principles were generated. Thereby, ways were demonstrated to control both ER and reproducibility of the etch behavior. A route for effective surface structuring by ER manipulation with the help of electron irradiation was pointed out. For the creation of efficient and reliable light sources for the modern world, no possibility for optimization should be skipped.

## Supplementary Measurement Data

Sample position	1	2	3	4	mean $\pm$ SDM (n = 4)
$S_q$ AFM	539	493	552	527	$528 \pm 22 \ (4 \%)$

**Table A.1:** Determined surface roughness  $S_q$  from AFM measurement in four individual positions on an identical GaN sample **A** (Figure 5.1) after etching in 30 wt. % aq. KOH solution at 80 °C for 6 min.

Sample position	1	2	3	4	5	mean $\pm$ SDM (n = 5)
$S_q$ WLI	1102	1084	763	605	1073	$925 \pm 204~(22~\%)$

**Table A.2:** Determined surface roughness  $S_q$  from WLI measurement in four individual positions on an identical GaN sample **A** (Figure 5.1) after etching in 30 wt. % aq. KOH solution at 80 °C for 6 min. The measurement coordinates are not equivalent to Table A.1. In comparison between AFM and WLI, an offset in absolute  $S_q$  was visible. Also the reproducibility of AFM measurement by means of the percentage SDM was higher. However, the power spectrum density was significantly different between WLI and AFM. Macroscopic effects (e.g., wafer bow) had a higher impact on WLI than on AFM.



Figure A.1: AFM image of single pyramid on GaN sample A after 6 min etching in 30 wt. % aq. KOH solution at 80 °C (left). The three contour lines mark cross sections of the pyramid side facets. Height diagram of three contour lines (right). Based on this measurement, the angle of the pyramid side facets relatively to the lateral base plane was determined to be  $61.5 \pm 0.6^{\circ}$ . The pyramid side planes could be identified as  $\{10\overline{11}\}$ crystal facets.



Figure A.2: PLM images of GaN wafers **D** (left) and **F** directly after epitaxial growth for determination of the absolute TD density. **D** and **F** had TD densities of  $> 4 \pm 10^8$  cm<sup>-2</sup> and  $1.1 \pm 10^8$  cm<sup>-2</sup>, respectively (mean  $\pm$  SDM, n = 5). These values were acquired by manual counting of dark spots in the PLM images. Due to cluster formation of dislocations, the value given in case of **D** represents a minimum value.



**Figure A.3:** SEM images of two positions on a single GaN sample surface **A** after polishing in alkaline slurry for 128 s. A uniform and smooth morphology was achieved, which was confirmed by an AFM determined  $R_q$  roughness of 1.1 nm.



Figure A.4: ICP-OES determined etch kinetics of 8 individual GaN samples C without (left) and with (right) polishing prior to etching in 30 wt. % aq. KOH solution at 60 °C. The samples were taken from random positions on each wafer, which led to significant material-dependent ER variation without polishing. Non-uniform LLO surface roughness was the reason for that. By polishing, on the other hand, the impact of material variation on the ER was almost entirely eliminated. This resulted in an increased reproducibility.



**Figure A.5:** SEM images of different positions on 6 inch GaN wafer **A** 4 (left and center) and 5 (right) after polishing and 3.5 min SAT etching in 30 wt. % aq. KOH at 60 °C. For wafer number reference see Table 6.6. (0001) plateaus were found effectively reducing the WLI determined  $S_q$  roughness.



Figure A.6: Cross-sectional SEM images of FIB cut GaN wafers A 3 (left), 4 (center) and 5 (right) after polishing and 3.5 min SAT etching in 30 wt. % aq. KOH at 60 °C. For wafer number reference see Table 6.6. Areas in which plateau formation had occurred were visible across the entire wafer. The remaining epitaxial layer thickness, which was almost identical in all cases, proved the plateau to be at the transition between 3D and 2D-2 GaN. The scale bar refers to all images.

#### Supplementary Measurement Data



Figure A.7: ICP-OES determined ERs of non-polished GaN A in 20-26 wt. % aq. KOH solution at 80 °C. Due to the lacking polishing step and the thereby caused ER variation, the slight difference in process control could not be resolved.

Т / К	ER / nm min <sup>-1</sup>	T <sup>-1</sup> / K <sup>-1</sup>	$\ln (ER / nm min^{-1})$
22	$12\pm1$	0.00339	$2.48\pm0.12$
30	$17\pm12$	0.00330	$2.85\pm0.83$
40	$34\pm11$	0.00319	$3.85\pm0.27$
50	$80\pm22$	0.00309	$4.38\pm0.29$
60	$258\pm26$	0.00300	$5.55\pm0.10$
70	$382\pm5$	0.00291	$5.95\pm0.01$
80	$868\pm35$	0.00283	$6.77\pm0.04$

**Table A.3:** ICP-OES determined ER of polished GaN **C** during etching in 30 wt. % aq. KOH solution at temperatures between 22 °C and 80 °C. The ER values were acquired by linear fits of the etch kinetics between 900 nm and 1600 nm average material removal z (GaN). The data was determined as mean  $\pm$  SDM (n = 5).



Figure A.8: EDX spectra of dark deposition on electron beam irradiated GaN ("dark section") and clean GaN ("bright section") after etching in 30 wt. % aq. KOH at 80 °C for 6 min. 5 kV acceleration voltage were used during EDX measurement. More pronounced carbon and oxygen peaks were observed in the dark section.



Figure A.9: Overview SEM image of GaN sample area A after 8 keV electron beam irradiation and etching in 30 wt. % aq. KOH at 80 °C for 6 min. From the spots referred to as sections 1-7, the spectra shown in Figure A.10 were recorded. The bright spots in the image correspond to GaN pyramids whereas the dark lines refer to the linear structures achieved by electron irradiation prior to etching.



Figure A.10: EDX spectra of dark carbon-containing deposition on electron beam irradiated GaN area A (Figure A.9) after etching in 30 wt. % aq. KOH at 80 °C for 6 min. Bright sections without deposits are included as a reference. 5 kV acceleration voltage were used during EDX measurement. A systematic difference in the C and O peaks between dark and bright sections could not be confirmed by this experiment. The occurrence of carbon and oxygen peaks in the spectra was randomly distributed.



Figure A.11: SEM overview images of GaN sample areas A after electron beam irradiation and etching in 30 wt. % aq. KOH at 80 °C for 6 min. In the spots referred to as 1-5, the spectra shown in the following were recorded. Directly on the electron beam irradiated sections 1-3 only carbon and oxygen were found after etching. Two reference sections 4-5 showed gallium and nitrogen peaks in addition to carbon and oxygen.



**Figure A.12:** AES spectrum of electron beam irradiated GaN surface 1 (Figure A.11) after etching in 30 wt. % aq. KOH at 80 °C for 6 min.



Figure A.13: AES spectrum of electron beam irradiated GaN surface 2 (Figure A.11) after etching in 30 wt. % aq. KOH at 80 °C for 6 min.



Figure A.14: AES spectrum of electron beam irradiated GaN surface 3 (Figure A.11) after etching in 30 wt. % aq. KOH at 80 °C for 6 min.



**Figure A.15:** AES spectrum of electron beam irradiated GaN surface 4 (Figure A.11) after etching in 30 wt. % aq. KOH at 80 °C for 6 min.



Figure A.16: AES spectrum of electron beam irradiated GaN surface 5 (Figure A.11) after etching in 30 wt. % aq. KOH at  $80 \degree \text{C}$  for  $6 \min$ .

# Abbreviations

- $\mathbf{1D} \ \mathrm{Onedimensional}$
- $2\mathbf{D}$  Two dimensional
- 3D Three dimensional
- **AES** Auger electron spectroscopy
- **AFM** Atomic force microscopy
- aq. Aqueous
- App. Appearance
- ${\bf CB}\,$  Conduction band
- ${\bf CL}$  Cathodoluminescence
- **CLM** Cathodoluminescence microscopy
- **CVD** Chemical vapor deposition
- **DIW** Deionized water
- EDX Energy dispersive x-ray spectroscopy
- ${\bf ER}~{\rm Etch}$  rate
- etc. etcetera
- ${\bf FIB}\,$  Focused ion beam
- **HVPE** Hydride vapor phase epitaxy

#### Abbreviations

**HWE** Hot wall epitaxy

**ICP-OES** Inductively coupled plasma-optical emission spectroscopy

**LED** Light emitting diode

 ${\bf LLO}~{\rm Laser}~{\rm lift-off}$ 

**MBE** Molecular beam epitaxy

MOCVD Metal organic chemical vapor deposition

 $\mathbf{MQW}$  Multi quantum well

**NMP** *N*-Methylpyrrolidone

org. Organic

p.a. Pro analysi

 $\mathbf{PEC}$  Photoelectrochemical

 $\mathbf{PL}$  Photoluminescence

**PLM** Photoluminescence microscopy

**PSS** Patterned sapphire substrate

 ${\bf RMS}\,$  Root mean square

SAT Spray acid tool

**SEM** Scanning electron microscopy

 ${\bf TD}\,$  Threading dislocation

 ${\bf TEM}\,$  Transmission electron microscopy

 $\mathbf{TMAl}\xspace$  Trimethyl aluminium

 $\mathbf{TMA^{III}}$  Trimethyl group-III element compound

 $\mathbf{TMGa}\,$  Trimethyl gallium

**TMIn** Trimethyl indium

 $\mathbf{UV}$  Ultraviolet

 ${\bf VB}\,$  Valence band

 ${\bf WIW}$  Within wafer

**WLI** White light interferometry

- ${\bf XRD}\,$  X-ray diffractometry
- $\mathbf{XPS}$  X-ray photoelectron spectroscopy

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## **Publications**

#### **Journal Papers**

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- Influence of Epitaxial Composition on N-Face GaN KOH Etch Kinetics Determined by ICP-OES, M. Tautz, M. T. Kuchenbrod, J. Hertkorn, R. Weinberger, M. Welzel, A. Pfitzner, D. Díaz Díaz, Beilstein J. Nanotechnol., 2020, 11, 41-50.
- Wet-Chemical GaN Etching on the Atomic Level: a Study of Mechanism and Anisotropy, M. Tautz, A. Weimar, C. Graßl, M. Welzel, D. Díaz Díaz, in preparation.

#### **Patent Applications**

1. M. Tautz, M. J. Davies, M. Welzel, DE102019106964.5, 19.03.2019.

#### Presentations

- 1. *ICP-OES als Grundlage für die Prozessevaluation beim nasschemischen Aufrauen von Galliumnitrid*, Thermo Fisher Anwendertreffen ICP-OES, Hannover, Deutschland, 09.-10.11.2017.
- Analyse des Galliumnitrid Ätzverhaltens in wässriger KOH Lösung mittels ICP-OES, ANAKON 2019, Münster, Deutschland, 25.-28.03.2019.

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