Impact of Electrochemical Process on the Degradation Mechanisms of AlGaN/GaN HEMTs

by

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ABSTRACT

AlGaN/GaN high electron mobility transistors (HEMTs) constitute a new generation of
transistors with excellent electrical characteristics and great potential to replace silicon
technology in the future, especially in high power and high frequency applications. However,
the poor long term reliability of these devices is an important bottleneck for their wide
market insertion and limits their advanced development. This thesis tackles this problem
by focusing on understanding the physics behind various degradation modes and providing new
quantitative models to explain these mechanisms.

The first part of the thesis, Chapters 2 and 3, reports studies of the origin of permanent
structural and electrical degradation in AlGaN/GaN HEMTs. Hydroxyl groups (OH⁻) from
the environment and/or adsorbed water on the III-N surface are found to play an important
role in the formation of surface pits during the OFF-state electrical stress. The mechanism of
this water-related structural degradation is explained by an electrochemical cell formed at the
gate edge where gate metal, the II-N surface and the passivation layer meet. Moreover, the
permanent decrease of the drain current is directly linked with the formation of the surface
pits, while the permanent increase of the gate current is found to be uncorrelated with the
structural degradation.

The second part of the thesis, Chapters 4 and 5, identifies water-related redox couples in
ambient air as important sources of dynamic on-resistance and drain current collapse in
AlGaN/GaN HEMTs. Through in-situ X-ray photoelectron spectroscopy (XPS), direct
signature of the water-related species is found at the AlGaN surface at room temperature. It is
also found that these species, as well as the current collapse, can be thermally removed above
200 °C in vacuum conditions. An electron trapping mechanism based on H₂O/H₂ and H₂O/O₂
redox couples is proposed to explain the 0.5 eV energy level commonly attributed to surface
trapping states. Moreover, the role of silicon nitride passivation in successfully removing
current collapse in these devices is explained by blocking the water molecules away from the
AlGaN surface. Finally, fluorocarbon, a highly hydrophobic material, is proven to be an
excellent passivation to overcome transient degradation mechanisms in AlGaN/GaN HEMTs.

Thesis Supervisor: Tomás Palacios
Title: Associate Professor of Electrical Engineering
Acknowledgement

I believe every Ph.D has a unique story to tell. So do I. Five years in a man’s precious 20s is dedicated in your beloved research. I will say it is definitely worth it. Putting me in the position five years ago when I first stepped in MIT campus, I totally cannot imagine what I have experienced and learned today. Along this long journey, I have become a more professional and more comprehensive person, thanks to helps from a lot of people. Here, I would like to express my deepest and sincerest gratitude to all of them. Firstly, I would thank my advisor Prof. Tomás Palacios, who is not only my thesis advisor but my life advisor as well. His sharp foresight in research, encouraging attitude and kindness always fuel me with more power and enthusiasm in my projects. Moreover, I have learned a lot from his professionals, team-playing and strong planning abilities. I cannot imagine a second person who can influence me that much during these five years. I sincerely feel lucky and grateful to be his student and will cherish this invaluable treasure in my life time.

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Chapter 1 Introduction

1.1 Introduction to AlGaN/GaN HEMTs

Since M. A. Khan, et al. [1] demonstrated the first AlGaN/GaN high electron mobility transistor (HEMT) in 1993, GaN-based technology has witnessed twenty years of exciting developments. GaN semiconductors have dramatically evolved from devices with less than 20 mA/mm of output current and virtually no high frequency performance, to devices with extremely high output power such as 250 W at 2.1 GHz [2] and 5.8 W at 40 GHz [3], high cut-off frequency $f_T = 450$ GHz at $L_g = 70$ nm [4], high-power efficiency $\text{PAE} = 99.3\%$ at $P_{\text{sat}} = 1500$ W [5], and world-wide commercialization [6].

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Silicon</th>
<th>AlGaAs/InGaAs</th>
<th>InAlAs/InGaAs</th>
<th>SiC</th>
<th>AlGaN/GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>1.1</td>
<td>1.42</td>
<td>1.35</td>
<td>3.26</td>
<td>3.3-4.2</td>
</tr>
<tr>
<td>Electron mobility at 300 K (cm$^2$/V·s)</td>
<td>1500</td>
<td>8500</td>
<td>5400</td>
<td>700</td>
<td>1500-2200</td>
</tr>
<tr>
<td>Saturated (peak) electron velocity ($10^7$ cm/s)</td>
<td>1.0 (1.0)</td>
<td>1.3 (2.1)</td>
<td>1.0 (2.3)</td>
<td>2.0 (2.0)</td>
<td>1.3 (2.1)</td>
</tr>
<tr>
<td>Critical breakdown field (MV/cm)</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>3.0</td>
<td>&gt; 3.0</td>
</tr>
</tbody>
</table>

Table 1-1. Basic electrical characteristics of various semiconductors: Silicon, AlGaAs/InGaAs, InAlAs/InGaAs, SiC and AlGaN/GaN materials.

The great development and extraordinary performance of AlGaN/GaN-based electronics are mainly attributed to the outstanding electronic properties of the AlGaN and GaN materials. Wide bandgap ranging from 3.3 eV to 4.2 eV makes these semiconductors stand more than ten times higher breakdown field ($> 3$ MV/cm) and breakdown voltage (e.g. 8300 V [7]) than Silicon. Strong piezoelectric and spontaneous polarization in III-Nitrides results in a 2-dimentional electron gas (2DEG) with a high sheet carrier density (normally 0.7-
1.4x10^{13} \text{ cm}^2) without any intentional doping. Moreover, the confined 2DEG between at the AlGaN/GaN interface gives rise to high electron mobility (> 1500 \text{ cm}^2/\text{V}\times\text{s} at room temperature) and high electron velocity (~2.5x10^7 \text{ cm/s} peak velocity and ~1.3x10^7 \text{ cm/s} saturated velocity [8]). The high electron mobility and carrier concentration of AlGaN/GaN structure allow the fabrication of AlGaN/GaN HEMTs with maximum drain current densities in excess of 2 A/mm [9]. The unique combination of both high current density and large breakdown voltage makes AlGaN/GaN HEMTs very promising among the top candidates for future power amplifiers. The electric characteristics of popular semiconductors including AlGaN/GaN are summarized in Table 1-1.

![Figure 1-1. Advantages of GaN-based power transistors respect to other semiconductors [10].](image)

Currently, AlGaN/GaN HEMTs have been commercially available for power amplification since 2005 in cell-phone base stations at 2 GHz and a total output power in excess of 280W have been reported at that frequency [11]. At 4 GHz, AlGaN/GaN HEMTs have demonstrated more than 40 W mm\(^{-1}\) of output power with a power added efficiency (PAE) of 60% at V_{ds} = 135 V [12]. This performance is more than one order of magnitude
better than those of any other competing semiconductor technology such as GaAs and InP as seen in Figure 1-1. In addition, the high electron velocity also makes AlGaN/GaN HEMTs one of the best candidates for very high frequency operation. A maximum current gain cutoff frequency \( f_T \) of 450 GHz was reported in AlGaN/GaN HEMTs with a gate length in the 20-30 nm range [13]. When biased for maximum power gain, these devices could reach 600 GHz of maximum power gain frequency \( f_{\text{max}} \) [13]. Therefore, the target markets of GaN-based devices are mainly related to high power and high frequency designs such as cellular infrastructure, broadband wireless access, radar and communications applications.

1.2 Thesis Motivation

After twenty years of high-speed development, the greatest challenge and focus of the GaN-based technology has already been shifted from breaking performance records or designing new device structures to achieving a high level of device reliability. After all, in terms of practice, only devices with reliable performance have commercial value. Several degradation modes have been found to limit the device performance of AlGaN/GaN HEMTs [14][15]. However, to date there has not been a consensus on the physical mechanisms nor a general solution to overcome the degradation issues. The main motivation of this thesis is therefore to provide a physics-based understanding of the specific GaN-related degradation mechanisms and to provide solution to improve the reliability of AlGaN/GaN HEMTs.

1.3 Reliability in AlGaN/GaN HEMTs

Years of research in the reliability of AlGaN/GaN HEMTs have recognized a variety of degradation phenomena, and as schematically shown in Figure 1-2, these degradation modes can be generally categorized into three main groups in terms of their physical nature [16]:

1. Thermally activated degradation modes, including the degradation of the metal contacts [17], self-heating [18], delamination of passivation layers [19], etc.

2. Hot-electrons-induced degradation modes including trapping effects caused by hot electrons trapped in deep levels of AlGaN and GaN bulk, interface and surface [20].
3. Specific GaN-related degradation modes including the inverse-piezoelectric degradation at the gate edge [14], defect generation due to the electro-thermo-mechanical failure [21], etc.

![Image](image.png)

**Figure 1-2.** Schematics representing the main mechanisms that can affect the reliability of GaN-based HEMTs [16].

The first two types of degradation mechanisms are also common in other semiconductor technologies such as Si, GaAs, SiC, etc. The third type is specific to GaN devices and is related to the following specific material and structural properties of the AlGaN/GaN device system:

1. The piezoelectric properties of GaN-related III-Nitride materials induce excess strain and stress under high applied electric field – the so-called inverse piezoelectric effect [22], which may cause mechanical breakdown and/or structural damage in devices.
2. The high electrical field that the bulk GaN semiconductor can sustain need to be also sustained by all the critical interfaces of the device including the 2DEG channel and the triple-line interface where the III-Nitride surface, gate metal and passivation layers meet.

In the following subsections, the previous work on understanding the degradation mechanisms specific to GaN technology will be briefly reviewed.

1.3.1 Inverse Piezoelectric Effect

Inverse piezoelectric effect is a property present on the hetero-structures in which the two atomic planes at each side of a hetero-interface display different electronegativity, such as the AlGaN and GaN layer in this case. The impact of the inverse piezoelectric effect mechanism in AlGaN/GaN HEMTs was first proposed by J. Joh, et al. in 2006 [23] to explain the phenomenon that in these devices there is exists a critical electric field below which negligible degradation is observed. Later, by utilizing the step-stress experimental methods under OFF-state, they found that the critical electric field is linked with a critical drain-to-gate voltage beyond which gate current start to suddenly increase and the output drain current starts to drop as shown in Figure 1-3 [24].

The sudden degradation of these devices beyond a critical electric field is explained by the mechanism of inverse piezoelectric effect because the applied electric filed changes the strain and stress distribution and thus the elastic energy density of the material. As the elastic energy reaches a specific material-defined limit, the mechanical energy in the semiconductor exceeds a threshold value and the material relaxes by generating cracks and other defects. The critical increase of gate current is therefore explained to be caused by these inverse-piezoelectric-effect-induced defects [25]. Experimental evidence from TEM investigation further shows the formation of structural defects and voids at the drain edge of the gate (where the electric field peaks) after the electrical stress [26]. We will show many of these TEM and SEM images in Chapters 2 and 3. However, the causation of the gate current degradation and the field-induced inverse piezoelectric effect in AlGaN/GaN HEMTs has been heavily discussed and argued in the past. There are several other theories that have been developed in parallel to explain the physical mechanism behind this fast and irreversible
degradation of the gate current. The following two subsections will briefly introduce and review the other two main proposed mechanisms.

![Graph](image)

Figure 1-3. Change in normalized $I_{D_{\text{max}}}$, $R_D$, $R_S$, $I_{G\text{stress}}$, and $I_{G\text{off}}$ as a function of stress voltage in a step-stress experiment in the $V_{DS} = 0$ state ($V_{DG} = 10-50$ V in 1-V step) [24].

### 1.3.2 Defect Percolation Process

This theory is first suggested by Marcon et al. in 2010 [27] and developed by Matteo Meneghini et al. in 2011 [21] for the degradation mechanism of AlGaN/GaN HEMTs. This theory is motivated by the experimental finding that the gate current degradation observed in GaN HEMTs is actually a time-dependent process and could occur even below the ‘critical voltage’ given sufficient stress time as shown in Figure 1-4 below [21].
Figure 1-4. Results of a constant-voltage reverse-bias stress test. The three graphs represent the variation of (a) gate current, (b) amplitude of the noise on gate current and (c) threshold voltage during stress time [21].

Furthermore, it was shown that defects with activation energy of approximately 0.5 eV are generated during the stress [28]. Based on these results, the proposed model claims that during the reverse-gate-bias or the OFF-state stress defects are generated within the AlGaN layer due to the high electric field. As the stress time increases, the density of these defects may reach a critical threshold resulting in a conductive path (percolation) between gate and the GaN buffer or channel, causing the permanent degradation of the gate current. The main weakness of this theory is that the defect generation process in the AlGaN barrier is not very clear and the detailed mechanisms of the field-induced formation of the point defects are still lacking.

1.3.3 Oxygen-related Mechanisms
It is well known that an insulating oxide layer of thickness 1-2 nm is present on AlGaN/GaN surface after conventional cleaning [29]. This so-called native oxide could have a strong influence on the Schottky barrier contact characteristics such as Schottky barrier height (SBH) on AlGaN/GaN devices [30]. Some authors [31] have argued from TEM images that this native oxides could be modified or consumed during the electrical stress. A correlation between the oxides/oxygen and device degradation was further found [26] by studying with Transmission Electron Microscopy (TEM) Energy-Dispersive X-ray (EDX) analysis the surface of pits formed during the high drain bias stress. O (oxygen) peak with high intensity was found in these experiments. Moreover, many studies have demonstrated the generation of traps with an energy level ranging from 0.5 eV to 0.6 eV in the transistor access region close to the drain edge of the gate after both ON-state and OFF-state stress [32][28][33]. Based on this evidence, a diffusion process of oxygen-related impurities has been proposed by Martin Kuball et al. [34] as an early stage of the degradation in AlGaN/GaN HEMTs. The diffusion of oxygen could occur along dislocations in the AlGaN and GaN layers, be enhanced by the inverse piezoelectric effect, or finally cause the pit and crack formation as shown in Figure 1-5. However, key evidence of the diffusion process and the detailed physical mechanisms underneath this field-induced degradation mode are still missing.

In parallel, P. Markaram et al. [35] postulated a possible field-induced oxidation or electrochemical etching process to explain the observable V-shape surface pits and the increase of oxygen content. In Chapter 2 and Chapter 3, we will further study this mechanism and formulate a more complete and quantitative theory for the structural and electrical degradations in AlGaN/GaN HEMTs.
Figure 1-5. Schematic of possible diffusion related degradation mechanisms of AlGaN/GaN HEMTs: (a) diffusion along dislocations, (b) diffusion enhanced by inverse piezo-electric effect and (c) pit formation following a prior diffusion process [34].

1.4 Trapping Effects in AlGaN/GaN HEMTs

Reliability studies typically focus on the permanent degradation of devices, that is degradation mechanisms that set a hard limit to the device lifetime. However, GaN devices suffer from both permanent degradation and transient degradation (devices degrade temporarily i.e. trapping transients phenomena), and both mechanism impact the performance of the device and should be part of device reliability studies. In fact, the distinction between permanent and transient degradation is not clear in many cases, as some hot-electron-induced degradation modes which have been categorized into the reliability
regime as shown in Figure 1-2 may still recover but with recovery time of hours or days [16]. Moreover, many permanent and transient degradation modes in AlGaN/GaN HEMTs are caused by similar physical mechanisms such as the high electric field, the formation of defects, etc. [16][15]. Therefore, in a broader sense, device reliability is strongly linked with the transient degradation, namely the trapping effects.

Trapping is not a new phenomenon for GaN technology. It has been being one of the most notorious barriers for many semiconductor electronics. Point defects, dislocations, impurities, surface states, etc. are very common types of defects that could capture electrons or holes and degrade the output performance of devices [36]. For AlGaN/GaN HEMTs, a variety of phenomena has been associated to trapping behaviors, such as current collapse, dynamic on-resistance, frequency-dependent transconductance dispersion, dynamic on-resistance, gate- and drain-lag transients, pulsed I-V compression and microwave power slump, to name a few [37]. Trapping centers that are residing in the GaN buffer layers and/or at the AlGaN surface are found to be primarily responsible for the degradation on transient performance of AlGaN/GaN HEMTs. Buffer traps are associated with the drain-lag transients and largely reduced in devices with conductive buffer layers and/or improving materials quality [38]. On the other hand, surface traps are proved to be highly related to the gate bias [39][40] and have more prominent impact on the device transient performance in GaN-based HEMTs than other similar electronics such as GaAs-based FET.

In recent years, significant efforts have been directed to understand and suppress surface trapping effects in AlGaN/GaN HEMTs. Up to date, the leading theory of surface trapping mechanism has utilized the concept of the virtual gate [39] to explain the output current drop in operations of microwave frequency. Surface passivation, especially silicon nitride (SiNₓ) passivation has been found to significantly suppress the formation of the virtual gate and reduce current collapse and other transient degradation mechanisms [41][42], although the reason for that is still not clear.

1.4.1 Virtual Gate Concept
The concept of the virtual gate was first introduced by R. Vetury, et al. [39] to explain the current collapse in AlGaN/GaN HEMTs. Current collapse is a transient degradation mechanism where the on-state conductance and maximum current of the device significantly degrade after the device has been in the OFF-state for some time. This phenomenon is typically characterized through pulsed I-V measurements as shown in Figure 1-6. Pulsed I-V measurements basically pulse the gate bias while sweeping the drain voltage. A more detail description can be found in Chapter 4. Since the typical AlGaN/GaN HEMTs are normally-on devices, a switch from OFF-state to ON-state means a switch from negative gate voltage to zero, or positive gate voltage.

![Figure 1-6. DC and pulsed I-V drain characteristic showing current collapse for AlGaN/GaN HEMTs with different passivation processes [36].](image)

According to the virtual gate theory, the negative gate voltage injects energetic electrons to the AlGaN surface. As schematically shown in Figure 1-7, these electrons are then assumed to be trapped in existing empty surface donor states, forming negative charges on the surface, which act as a parallel reverse-biased gate and thus extending the depletion region. When the gate is switched back to the ON-state, the electrons trapped on the surface would be detrapped but with some level of time delay, which means that the 2DEG channel
is still partly depleted in ON-state when the switching is sufficiently fast. This delay between the electron trapping-detrapping and the gate voltage switching processes induce the collapse of the output current, that is a significant drop in the maximum current measured immediately after switching as compared to measurements performed in quasi-static conditions.

The virtual gate theory described above also explains the reason why passivation could prevent transient degradation. The passivation layer and/or the deposition process of the passivation layer buries and/or deactivates the surface donors and makes them inaccessible to electrons leaking from the gate [39]. In spite of the success of this theory in explaining the experimental evidence, there is still controversy on the detailed mechanisms by which the passivation prevents the formation of the virtual gate, which limits the optimization of the passivation layer.

Figure 1-7 Model of the device showing the location of the virtual gate and schematic representation of the device including the virtual gate [39].

1.5 Thesis Goal and Outline

The goal of this thesis is to provide a complete physical understanding of the permanent and transient degradation mechanisms that impact AlGaN/GaN HEMTs, namely the surface pitting and the surface trapping. The remainder of the thesis is organized as follows:
Chapters 2 and 3 focus on the study of the permanent degradation mechanisms of AlGaN/GaN HEMTs. In Chapter 2, the important role of oxygen during the reverse-gate-bias stress on the GaN HEMTs is addressed. Oxide particles and surface pits are found to form along the gate edge of stressed devices. This oxidation process is strongly dependent on the duration of the electrical stressing, the electric field and the environment.

In Chapter 3, a new mechanism related to water-assisted electrochemical reactions on the III-Nitride surface is proposed to explain the formation of surface pits during the electrical stress. Associated permanent electrical degradations including gate current increase and drain current drop are also systematically investigated and analyzed for their possible origins.

Chapters 4 and 5 study the origin of the transient degradation mechanisms in AlGaN/GaN HEMTs. In Chapter 4, ambient moisture has been identified as a previously unrecognized cause of current collapse in AlGaN/GaN HEMTs. Unpassivated devices exposed to dry air or protected with a hydrophobic passivation, such as vapor-deposited fluorocarbon, showed negligible current collapse. The use of a hydrophobic passivation to prevent DC-to-RF dispersion works even when it is not directly in contact with the semiconductor surface, which allows the engineering of multi-stack passivation layers to eliminate current collapse while minimizing parasitic capacitances.

In Chapter 5, a new mechanism related to water reduction-oxidation-reactions (redox) couples in ambient air is proposed to explain the physical nature of the surface trapping effects including the dynamic on-resistance and current collapse in AlGaN/GaN HEMTs. The success of SiNₓ passivation in limiting the surface trapping effects has also been well explained in the framework of this new mechanism.

Finally, in Chapter 6, conclusions are made and future work is presented.
Chapter 2 Role of Oxygen in Permanent GaN HEMT Degradation

2.1 Introduction and Motivation

AlGaN/GaN high electron mobility transistors (HEMTs) are very promising semiconductor devices for high power and high frequency applications [8]. The unique combination of high critical electric field, large polarization fields and high electron mobility allows AlGaN/GaN transistors to handle more than one order of magnitude higher power densities than any other semiconductor technology. However, the high electric field in the AlGaN/GaN HMETs is like a two-edged sword. In spite of the excellent power performance demonstrated by these devices, full market insertion is still limited by their poor reliability caused by various high field induced degradation modes [15].

In previous research, it has been observed that high drain voltage stress tests could cause pits and/or cracks in the region of the device exposed to large electric fields, which is mainly around the gate edge. The surface pits formed during the high drain bias stress were first found by U. Chowdhury, et al in [43] (Figure 2-1).

Figure 2-1. Cross-sectional HREM shows the formation of pits on both the source- and drain-side edges of the gate on 40-V drain bias stressed AlGaN/GaN HEMTs [43].
This surface pitting phenomenon has been linked to various degradation modes such as defect generation, current collapse and increased gate leakage currents [20]. Although the physics responsible for this permanent structural degradation in GaN HEMTs are still not very well understood [14][44], one of the most-accepted hypotheses has attributed the origin of this structural degradation to the large mechanical stresses induced by the combination of the large electric fields present in the AlGaN layer during the high drain bias stress test and the large inverse piezoelectric effect of nitride semiconductors [14]. The inverse piezoelectric effect in the AlGaN layer is schematically shown in Figure 2-2 below.

Figure 2-2. Inverse piezoelectric effect at the gate edge in the drain side of GaN HEMT. The vertical and horizontal arrows represent vertical electric field and mechanical stress, respectively [22].

In this and the next chapter, we will propose another new hypothesis that quantitatively explains the mechanisms of the structural degradation and also its relationship with the permanent electrical degradations. The next few sections of this Chapter present experimental evidence of the strong role of oxygen diffusion and field-driven oxidation in the structural degradation of GaN-based transistors for the first time. It also demonstrates how the high electric field induced in reverse-gate-bias stress experiments can cause the electrochemical oxidation of the AlGaN/GaN HEMTs surface at room temperature. Chapter 3 provides further experimental results so that we can build a more complete and quantitative
theory to understand the permanent degradations of AlGaN/GaN HEMTs including surface pitting, drain current decrease and gate current increase.

2.2 Device Structure

The devices studied in this work are fabricated on AlGaN/GaN heterostructures grown on 4H-SiC substrates using plasma-assisted molecular beam epitaxy (PAMBE). The thickness of the AlGaN layer is 30 nm and the GaN buffer layer is 2 μm thick. The Al component in the AlGaN layer is around 0.25. AlGaN/GaN HEMTs are fabricated on these samples using standard fabrication technology. Ohmic contacts are formed through Ti/Al/Ni/Au metallization and annealed at 870 °C in N₂ gas. A Ni/Au/Ni metal stack is used for the gate contact. The devices are passivated with a 12-nm-thick Al₂O₃ layer deposited by atomic layer deposition (ALD) before the formation of the gate, so the thin Al₂O₃ layer also serves as a gate oxide [45]. All the devices in this study have identical geometries, with a gate length of 2.5 μm, a gate-to-source/drain distance of 1.5 μm, and a gate width of 75 μm. The device structure is schematically shown in Figure 2-3 below.

Figure 2-3. Schematic of the structure of the AlGaN/GaN HEMTs studied in this work.
2.3 Experiments

2.3.1 Surface Particles and Surface Pits

Fresh devices were stressed under reverse gate bias conditions ($V_{ds} = 0$ V and $V_{gs} = -40$ V) for 6 s, 60 s, 600 s and 6000 s at room temperature in atmosphere.

![Images of AlGaN/GaN HEMTs stressed at $V_{ds} = 0$ V and $V_{gs} = -40$ V for different times.](image)

Figure 2-4. Top-view scanning electron microscope (SEM) images of AlGaN/GaN HEMTs stressed at $V_{ds} = 0$ V and $V_{gs} = -40$ V for 6 s (a), 60 s (b), 600 s (c), and 6000 s (d).

Figure 2-4 shows scanning electron microscopy (SEM) images of the surface morphology of the stressed transistors, as a function of the stress time. Elongated particles (stringers) are for the first time observed on the device surface, along the gate edge in both the gate-to-drain and gate-to-source access regions, as shown for stress durations above 60 s in Figure 2-4 (c) and (d). Due to the time evolution feature of this phenomenon, it seems that the particles grow during the OFF-state electrical stressing. The chemical composition of these particles was determined by using Auger electron spectroscopy (AES). The results are shown in Figure 2-5 below.
Figure 2-5. Auger Electron Spectra results (b) for three different regions of the transistor surface (a).

As it can be seen in Figure 2-5 (b) that gallium, aluminum and oxygen peaks are clearly identified on the surface of the particles (red line). AES spectra of the gate metal area (blue line) and of the Al$_2$O$_3$-passivated AlGaN surface (cyan line) far away from the particles are also obtained as references to show that the Ga peak is not because of contamination. Figure 2-5 (a) indicates the corresponding areas on an SEM image of the interesting region. Carbon
contamination is observed in all three areas, and is considered as an artifact of the microscopy technique. One of the most intriguing features of the AES spectra is the existence of gallium peak in the particles, which seems to have moved through or broken out of the Al$_2$O$_3$ passivation layer from the AlGaN or even GaN layers underneath. Another interesting characteristic of the AES spectra is higher concentration of oxygen found in the particles compared to other surface regions, which implies a possible oxidation process of the nitride semiconductor surface along the edge of the gate. The analysis of the atomic concentration obtained from the AES results further suggests that the ratio of the gallium and aluminum concentrations to the amount of oxygen in the particles is close to 2:3, which would be consistent with the formation of Ga$_2$O$_3$ and Al$_2$O$_3$. All of the findings above provide strong experimental evidence of a possible mass transport process during the OFF-state degradation in AlGaN/GaN HEMTs. We will observe this process more clearly and quantitatively in Chapter 3 when we show it with electrochemical reactions.

A close look at Figure 2-4 (d) reveals that there are pits associated with each particle or stringer on the surface. To show the surface pits clearly, the gate metals were removed by aqua regia etching (HCl : HNO$_3$, 3:1) for 20 min. The samples were subsequently cleaned using a piranha solution (H$_2$SO$_4$ : H$_2$O$_2$, 3:1) for 10 min, rinsed in deionized (DI) water for 1 min and dried using an N$_2$ gun. SEM measurements after the removal of gate metals and oxides confirm the relationship between particles and surface pits. Figure 2-6 shows a one-to-one match between particles and surface pits on an identical region. It seems very likely that the mass missing in each surface pit forms the associated surface particles.

In addition to the obvious large pits underneath the particles, there are also small pits distributed along the gate edge. Atomic force microscopy (AFM) measurements (Figure 2-7) indicate that the average depth of the large pits is 45 nm, and 25 nm for the small pits. All the AFM measurements done in this thesis were operated on Veeco Metrology Nanoscope V Scanned Probe Microscope (SPM) under the tapping mode. We believe these two sizes of surface pits have the same physical origin that is related with some oxidation process on the nitride semiconductor surface. In fact, in 2009, S.Y. Park, et al [26] have indicated that there was oxygen found inside the pits through TEM investigations, however, they did not look
into that further. In Chapter 3, we will show that the oxygen in the surface pits is, at least partially, originated from the water molecules in air.

Figure 2-6. Top-view SEM images of an AlGaN/GaN HEMT stressed at $V_{ds}=0V$ and $V_{gs}=-40V$ for 6000s before (a) and after (b) removal of the gate.
The structural degradation observed so far is driven by the voltage bias applied during the electrical stressing. The position of maximum electric field simulated on this device structure under the bias condition of $V_{ds} = 0$ V and $V_{gs} = -40$ V coincides with the pitting location – the edge of the gate as shown in Figure 2-8. Since the bias condition is symmetric referring to the source and the drain, the distribution of the surface pits is also symmetric.
In order to demonstrate the important role of the electric field in the structural degradation more clearly, we apply an asymmetric OFF-state bias such as $V_{ds} = 30$ V and $V_{gs} = -12$ V on the device, where the electric field peak is now located at the drain edge of the gate. The SEM image of the surface morphology of this device after the removal of the gate also only shows the formation of the pits on the drain side of the gate edge (Figure 2-8 (a)). In fact, the position of the surface pits at one side or the other of the gate can be changed by switching the source and drain voltages from $V_{ds} = 30$ V and $V_{gs} = -12$ V to $V_{sd} = 30$ V and $V_{gd} = -12$ V, as shown in Figure 2-8 (b). They always appear where the electric field is maximum. Moreover, it seems that there is a critical electric field and/or a correspondingly critical drain-to-gate/source-to-gate bias above which the surface pitting can occur, because
no surface pits are observable in SEM measurements at one side of the gate edge where the voltage drop is only 12 V. In Chapter 3, we will see that this critical electric field is hypothesized to be linked with the onset of the hole generation in the AlGaN layer through inter-band tunneling.

2.3.2 Role of Environment

The role of oxygen in the structural degradation is further studied by repeating the electrical stressing experiments in vacuum. A device, adjacent to the one used in the above experiments, was stressed under the same bias condition at \( V_{ds} = 0 \) V and \( V_{gs} = -40 \) V for 6000 s in a vacuum probe station with a residual vacuum of \( 3 \times 10^{-5} \) Torr. After stress, the large particles and surface pits observed in Figure 2-6 (a) and (b) do not appear when the device is top-view imaged in SEM as shown in Figure 2-9 (a) and (b). However, the smaller pits that form right at the edge of the gate electrode are still observed. The inset of Figure 2-9 (b) shows a zoom-in SEM image of the smaller pits. The disappearance of the particles and pits on devices stressed in vacuum further suggests the hypothesis that the particles and pits are caused by an electric-field-induced oxidation process occurred on the device surface. During the electrical stressing, oxygen from the atmosphere diffuses through the thin Al\(_2\)O\(_3\) passivation layer and locally oxidizes the AlGaN and/or GaN layer at high field region. We will see more details of this oxidation process in Chapter 3.
2.3.3 Electrical Degradation

Besides the surface morphology, the gate leakage and drain current are also monitored in all measurements as in [27][46]. After electrical stress, the gate leakage current at $V_{ds} = 0$ V increases in the samples stressed both in air (red solid line) and in vacuum (pink dashed line) conditions compared to fresh devices (blue dotted line) as shown in Fig. 2-10 (a). On the other hand, the reduced structural degradation of the sample stressed in vacuum results in a lower permanent degradation of the saturated drain-to-source current at $V_{ds} = 5$ V ($I_{dss}$) (as
seen in Fig. 2-10 (b)). In addition, a positive 4 V shift in the threshold voltage is observed for all the stressed samples (on inset of Fig. 2-10 (b)).

Therefore, it seems that the gate leakage current increase is unrelated to the particles and pits formation. However, these particles and pits created on the surface are, at least partially, responsible of the permanent drain current degradation. The localized oxidation along the gate edge might also consume oxygen from the intrinsic gate oxide or nearby Al₂O₃. The damage or thinning on the gate oxide (Al₂O₃ here) would modify the surface potential and mechanical stress, causing the observed positive shift of the threshold voltage. We will see later in Chapter 3 that there is no threshold voltage shift for Schottky gate devices (i.e. without gate oxide) after electrical stress, while surface pits are still created at the gate edge. It is because that the oxidation process can still consume oxygen from the atmosphere. The relationship between the electrical and structural degradations will also be demonstrated in more details in Chapter 3.

2.4 Conclusions
The experimental results described in this chapter show that oxygen can play an important role in the structural degradation of GaN-based transistors due to an electric-field-induced oxidation of the nitride semiconductor layer. Although in commercial samples the diffusion of oxygen from air might be slowed down by thick passivation layers and packaging (we will also quantitatively discuss this point in Chapter 3), there is always residual oxygen inside the semiconductor layers and, especially at the surface where previous report has identified a 1-2 nm layer of native oxide [15]. Given the presence of oxygen on the surface of almost every GaN transistor, our results suggest that the physical and electrical degradation observed in AlGaN/GaN HEMTs stressed in the reverse gate bias is, at least partially, due to the chemical oxidation of the nitride semiconductor surface, enhanced by the very high electric fields and enabled by the presence of oxygen in the form of a native oxide and/or from the atmosphere. This oxidation process may also be accelerated by the presence of native or piezoelectric-induced surface defects, or by a high density of charged nitrogen vacancies [47][48] near the surface. The oxide formation could assist or accelerate the breaking of Al/Ga-N bonds and generate nitrogen vacancies or nitrogen gases, which might further accelerate the oxidation of the AlGaN surface. In commercial samples with field-plate structures (and therefore a lower electric field around the gate edges) and thick passivation layers (and therefore a reduced oxygen supply), the oxidation process is limited to small pits and/or grooves as previously reported in [35], which is also the case in Chapter 3 when we use commercial AlGaN/GaN HEMTs. In samples without a field-plate (higher electric field at the gate edges) and thin passivation layers (increased oxygen supply) such as the devices studied in this work, the surface particles and pits that result from the oxidation process are much larger and can even break through the thin passivation layer, causing severe physical damage.

In summary, oxide particles and associated surface pits have been found for the first time on the surface of AlGaN/GaN HEMTs stressed in the reverse gate bias at room temperature in air. These particles/pits appear along the gate edges of the transistors, where the electric field is maximum. The chemical composition of these particles is consistent with a combination of Ga$_2$O$_3$ and Al$_2$O$_3$, as shown by Auger Electron Spectra. The important role of oxygen in this oxidation process has been proven both from the high oxygen concentration detected in particles and through stress tests in vacuum, where the structural and electrical
degradations are significantly reduced. The critical role of the electric field has been demonstrated by the finding that the particles and pits always form on the high-field side of the gate, for different stressing conditions. Based on the discovery of oxidation particles and the associated surface pit in addition to the time dependence and critical electric field features, a complete theory of electric-field-driven electrochemical reactions on the III-Nitride surface at the edge of the gate will be proposed later in Chapter 3. This theory explains the mechanisms of the surface pitting and its relationship with the permanent electrical degradations in AlGaN/GaN HEMTs.

The work of this Chapter has been partially published in [49].
Chapter 3 Electrochemical Reactions in Reliability

3.1 Introduction and Motivation

Most of the reliability issues in AlGaN/GaN HEMTs are related to the electric field in the AlGaN barrier and/or in the channel region, which can usually exceed 2 MV/cm [8] under high drain bias. The impact of the electric field on the device reliability is especially significant in the OFF-state when the channel is pinched off and the electric field is the highest.

The main structural degradation mechanisms studied to date for AlGaN/GaN HEMTs are related to the formation of physical defects (pits and cracks) during high drain OFF-state stress, and the electrical degradations are categorized into two failure modes: the gate current ($I_g$) increase and the drain current ($I_d$) drop. It has been argued in the past that the field-induced inverse piezoelectric effect of AlGaN material may play a role in causing surface cracking and $I_g$ degradation above a critical gate voltage [24]. In parallel, it has also been reported that the electrical degradation can occur even below the critical gate voltage given enough stress time due to a defect percolation process [21][50][27][28]. Moreover, the pits could also be caused by electrochemical reactions at the surface due to the combination of high electric field and oxygen [35][49], as we have discussed in Chapter 2. Despite these proposed degradation models, direct experimental evidence of the nature of the structural and electrical degradation in AlGaN/GaN HEMTs are still lacking.

In order to fully understand the permanent degradation mechanisms of AlGaN/GaN HEMTs, based on the findings described in Chapter 2, more systematical investigations of device degradation have been carried out in a precisely controlled ambient. In this work, we have found a close relationship between air moisture and surface pitting as demonstrated in Section 3.3. Based on this observation, a water-assisted corrosion-like electrochemical reaction is proposed to explain the mechanism, which is discussed in details in Section 3.4. The two necessary conditions for this electrochemical process to occur – the presence of hole carriers and water – are supported by experimental and theoretical evidence in Section 3.5 and 3.6, respectively. Moreover, we also find a one-to-one correlation between the drain...
current degradation and the surface pit formation. However, on the other hand, no correlation is found with the gate current degradation. Therefore we suggest different mechanisms for the two electrical degradation modes in Section 3.7. The results described in this study have been reproduced in more than 75 devices across 15 different wafers, both from industry and academia, to achieve statistical generality.

3.2 Device Structure and Experimental Setup

Prototype AlGaN/GaN HEMTs made by an industrial collaborator are used in this study. Similar results are achieved in transistors fabricated at MIT as have been demonstrated in Chapter 2. The HEMT structure consists of a 3 nm GaN cap, 14 nm AlGaN barrier, 1 nm AlN interlayer and a thick GaN buffer layer epitaxially grown on a semi-insulating substrate. An Lg = 250 nm T-shaped Pt/Au gate is deposited via metal evaporation. The device surface is passivated by a thick SiNy layer deposited using plasma enhanced chemical vapor deposition (PECVD). The device structure is schematically shown in Figure 3-1.

![Figure 3-1. Schematic of the structure of the industrial AlGaN/GaN HEMTs studied in this work.](image)

All the experiments were performed in a vacuum probe station. This vacuum probe stations is equipped with four metal probes, an optical window, a thermal chuck that can be
heated up to 500 °C (we will see the use of it in later chapters) and two gas lines. The gases could be introduced into the chamber in a controlled way by using the mass flow controllers (MFCs). Figure 3-2 below shows the real setup in left and a schematic in right.

Figure 3-2. A vacuum probe station used in this work. Left figure shows the real setup and the right figure shows a schematic.

### 3.3 Experiments

Two chips from the same wafer with five identical AlGaN/GaN HEMTs on each chip were stressed at high drain OFF-state bias ($V_{gs} = -7$ V and $V_{ds} = 43$ V) for 3000 s (at room temperature in darkness), one in ambient air and the other in a $1 \times 10^{-7}$ Torr vacuum. The drain and gate current characteristics are first recorded for each fresh transistor and then measured again after electrical stress. To ensure that the after-stress measurements are not influenced by trap-related transients, before the measurements the devices are illuminated for one minute with ultraviolet (UV) light (254 nm) and kept at rest for 12 hour to fully eliminate trapping transients. As summarized in Table 3-1, a small decrease in the drain saturation current $I_{ds}$ and an increase in the drain resistance $R_d$ are observed in HEMTs stressed in ambient air and the degradation is less in HEMTs stressed in a vacuum. Threshold voltage $V_T$ showed no shift after stress in both cases.
AlGaN/GaN HEMTs stressed in ambient air

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<tr>
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<th>Before Stress</th>
<th>After Stress</th>
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<tbody>
<tr>
<td>$I_{dss}$ (mA/mm)</td>
<td>766</td>
<td>728</td>
</tr>
<tr>
<td>$I_g$ (mA/mm)</td>
<td>$5.08 \times 10^{-6}$</td>
<td>1.40</td>
</tr>
<tr>
<td>$V_T$ (V)</td>
<td>-2.98</td>
<td>-3.01</td>
</tr>
<tr>
<td>$R_d$ ($\Omega \cdot$mm)</td>
<td>3.74</td>
<td>4.07</td>
</tr>
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AlGaN/GaN HEMTs stressed in vacuum

<table>
<thead>
<tr>
<th></th>
<th>Before Stress</th>
<th>After Stress</th>
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<tbody>
<tr>
<td>$I_{dss}$ (mA/mm)</td>
<td>760</td>
<td>756</td>
</tr>
<tr>
<td>$I_g$ (mA/mm)</td>
<td>$9.88 \times 10^{-6}$</td>
<td>0.924</td>
</tr>
<tr>
<td>$V_T$ (V)</td>
<td>-2.99</td>
<td>-2.99</td>
</tr>
<tr>
<td>$R_d$ ($\Omega \cdot$mm)</td>
<td>3.76</td>
<td>3.90</td>
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$I_{dss}$ and $I_g$ are measured at $V_{gs} = 0$ V and $V_{ds} = 5$ V. The measurements were carried out in ambient air at room temperature and in the dark.

Table 3-1. Electrical characteristics of AlGaN/GaN HEMTs stressed in ambient air and in vacuum.

The gate currents before, during and after the OFF-state stress are also measured as a function of the stress time. As shown in Table 3-1 and Figure 3-3, $I_g$ degrades by several orders of magnitude right after the very first stress point (i.e. in 1 ms) and does not vary much during continued stressing for devices stressed in both air and vacuum (with ~ 10% errors). The during-stress gate currents are also shown in the inset of Figure 3-3 and these values will play a role in quantitatively examining the mechanisms of the surface pitting, to be discussed in Section 3.5.

The mechanisms behind the above electrical degradation will be further discussed in Section 3.7.
Figure 3-3. Ratio of after-stress gate current ($I_{g,\text{stressed}}$) and unstressed gate current ($I_{g,\text{fresh}}$) at $V_{gs} = 0$ V and $V_{ds} = 5$ V as a function of stress time from 1 ms up to 10000 s. The AlGaN/GaN HEMTs were stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V in ambient air (red circles) and in a vacuum of $1 \times 10^{-7}$ Torr (blue triangles). The inset shows the during-stress gate current ($I_{g,\text{in-stress}}$) for these devices.

After electrical stressing, the two HEMT chips are subjected to a wet etching process to expose the GaN surface under the gate. The SiNy passivation is removed by HF etching (HF : H$_2$O, 1:10) for 2 min; gate metals are removed by aqua regia etching (HCl : HNO$_3$, 3:1) for 20 min and the samples are subsequently cleaned using a piranha solution (H$_2$SO$_4$ : H$_2$O$_2$, 3:1) for 10 min, rinsed in deionized (DI) water for 1 min and dried using an N$_2$ gun.
After the removal of the gate metal, the exposed surfaces in the gate area of these electrically-stressed HEMTs are investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 3-4 shows the top view and depth profile of the surface area around the gate of the HEMTs that are stressed in ambient air and in vacuum. It can be seen that the mean size and density of the surface pits are significantly higher in the HEMTs stressed in ambient air than those stressed in vacuum. These results are consistent among the five devices studied in each chip, and reinforce our previous observations (Figure 2-6 in Chapter 2) on AlGaN/GaN HEMTs fabricated at MIT. It is worth noting that the wet etching process does not attack the semiconductor, and an unstressed identical HEMT on the
same wafer shows a smooth surface around the gate area (not shown), confirming that the surface pitting observed in the AFM analysis is indeed caused by electrical stressing.

Figure 3-5. Cross-sectional TEM images at the drain edge of the gate in the AlGaN/GaN HEMTs stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V for 3000 s in ambient air (a) and in a vacuum of $1 \times 10^{-7}$ Torr (b); EDX line analysis across the pitting area for the above HEMTs stressed in ambient air (c) and in vacuum (d). The EDX line scan is indicated as the yellow line in (a) and (b).

A different set of two HEMTs (one in each chip) is imaged using cross-sectional transmission electron microscopy (TEM) to study the pits without etching the passivation and gate metals. The TEM samples were prepared in the following ways:
a) Two mirror trenches were etched on both sides of the cross-sectional view of the device and a U-cut was etched into the lamella with focused ion beam;

b) The omni-probe was lowered to touch the lamella and welded with a Pt source;

c) The lamella was freed from the substrate by etching the top portion of the lamella with focused ion beam;

d) The lamella was lifted up and transferred to the TEM grid and welded with Pt source;

f) Thinned down the lamella to 100nm until it is transparent to electron beams.

The TEM images were obtained from JEOL 2010F. All the TEM images were obtained under bright field mode and the STEM EDX were done in dark field mode.

A smaller pit size is again found in the devices stressed in vacuum compared with those stressed in ambient air as shown in Figure 3-5 (a) and (b), respectively. In addition, the material in the surface pits is characterized using EDX. A low concentration of gallium and aluminum and a high concentration of oxygen are observed inside the pit, as shown in Figure 3-5 (c) and (d). The important role of oxygen in the structural degradation of AlGaN/GaN HEMTs is therefore reinforced by using EDX measurements.

Given that surface pitting is reduced when the devices are electrically stressed in vacuum conditions, the oxygen in the pits is most likely from the oxygen gas O₂ and/or moisture H₂O present in ambient air. In order to discriminate between these two options, another two chips of five identical AlGaN/GaN HEMTs are stressed in the chamber at the same OFF-state bias and duration conditions as above in water-saturated Argon gas and in dry Argon gas. To saturate the Argon gas with water, Ar is passed through a deionized (DI) water bubbler at room temperature to the gas line of the vacuum probe station, so that the humidity of the whole chamber is very close to 100%. The dry Ar atmosphere is achieved by flowing argon gas through a drying unit which could lower the humidity to less than 1%.

Large $I_{ds}$ and $R_d$ degradation are observed in HEMTs stressed in water-saturated Ar and a significantly lower degradation is observed in HEMTs stressed in dry Ar. However, $I_g$ degradation is significant in both cases. No change of $V_T$ is found in both cases. All the
electrical characteristics are recorded in Table 3-2. Detailed discussion on the electrical degradation observed can be found in Section 3.7. In addition, the during-stress gate currents are also recorded and, as in the air and vacuum experiments, all change in $I_g$ happened at the first stress point (in 1 ms), beyond which $I_g$ does not change much during the continued electrical stressing.

<table>
<thead>
<tr>
<th>AlGaN/GaN HEMTs stressed in water-saturated Ar</th>
<th>Before Stress</th>
<th>After Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{ds}$ (mA/mm)</td>
<td>794</td>
<td>565</td>
</tr>
<tr>
<td>$I_g$ (mA/mm)</td>
<td>$3.79 \cdot 10^{-5}$</td>
<td>2.04</td>
</tr>
<tr>
<td>$V_T$ (V)</td>
<td>-2.99</td>
<td>-3.00</td>
</tr>
<tr>
<td>$R_d$ ($\Omega \cdot \text{mm}$)</td>
<td>3.66</td>
<td>5.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>AlGaN/GaN HEMTs stressed in dry Ar</th>
<th>Before Stress</th>
<th>After Stress</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{ds}$ (mA/mm)</td>
<td>762</td>
<td>759</td>
</tr>
<tr>
<td>$I_g$ (mA/mm)</td>
<td>$1.12 \cdot 10^{-5}$</td>
<td>0.808</td>
</tr>
<tr>
<td>$V_T$ (V)</td>
<td>-2.99</td>
<td>-3.00</td>
</tr>
<tr>
<td>$R_d$ ($\Omega \cdot \text{mm}$)</td>
<td>3.73</td>
<td>3.90</td>
</tr>
</tbody>
</table>

$I_{ds}$ and $I_g$ are measured at $V_{ds} = 0 \text{ V}$ and $V_{ds} = 5 \text{ V}$. The measurements were carried out in ambient air at room temperature and in the dark.

Table 3-2. Electrical characteristics of AlGaN/GaN HEMTs stressed in water-saturated Ar and in dry Ar.

After stressing, the gate metal and passivation layers are removed as described above, and the exposed surface is subsequently analyzed using SEM. At the same time, several devices in each chip, that are not wet etched, are investigated using cross-sectional TEM. As shown in Figure 3-6., the surface pitting is significantly accelerated by water-saturated Ar with respect to dry Ar.

The difference in the pit sizes between water-saturated and dry Ar gas is also reproducible in other gas environments including air, oxygen gas ($O_2$), nitrogen gas ($N_2$) and
carbon dioxide gas (CO\textsubscript{2}). More importantly, the suppressed surface pitting phenomena observed on devices stressed in dry air, dry oxygen gas and dry carbon dioxide gas provide strongly supportive evidence for the hypothesis that the oxygen observed in the pitting area is in fact originated from water molecules/moisture in the atmosphere. This finding smoothens the way for us to quantitatively formulate the related electrochemical reactions on the surface of the nitride semiconductors. The following Section will provide more details.

Figure 3-6. SEM images of AlGaN/GaN HEMTs stressed at \( V_{gs} = -7 \) V and \( V_{ds} = 43 \) V for 3000 s in water-saturated Ar (a) and in dry Ar (b), after gate metals and passivations were removed; Cross-sectional TEM images at the drain edge of the gate in AlGaN/GaN HEMTs stressed in water-saturated Ar (c) and in dry Ar (d) before etching.
3.4 Water-assisted Electrochemical Reactions

Previous work has found that ambient moisture corrodes GaAs, causing subsequent device degradation [51][52]. In this study, we propose that a water-assisted electrochemical reaction or corrosion process is a significant contributor of the surface pitting observed after OFF-state degradation in AlGaN/GaN HEMTs. The gate-SiNy-Al\textsubscript{x}Ga\textsubscript{1-x}N region at the gate edge forms an electrochemical cell which causes anodic oxidation of the Al\textsubscript{x}Ga\textsubscript{1-x}N layer (as illustrated in Figure 3-7). The reaction starts at the GaN cap surface and then proceeds into the AlGaN barrier during the electrical stress. For simplicity, we use Al\textsubscript{x}Ga\textsubscript{1-x}N to indicate both the GaN cap (x=0) and the AlGaN barrier. The proposed reduction-oxidation (redox) reaction between Al\textsubscript{x}Ga\textsubscript{1-x}N and water is:

\[ 2\text{Al}_x\text{Ga}_{1-x}\text{N} + 3\text{H}_2\text{O} = x\text{Al}_2\text{O}_3 + (1-x)\text{Ga}_2\text{O}_3 + \text{N}_2 \uparrow + 3\text{H}_2 \uparrow. \] (3.1)

The gate-SiNy-Al\textsubscript{x}Ga\textsubscript{1-x}N triple-line at the gate edge forms an electrochemical cell which causes anodic oxidation of the Al\textsubscript{x}Ga\textsubscript{1-x}N layer. This cell is schematically drawn on the TEM image of the surface pitting area in Figure 3-7.

In the electrochemical cell, the gate metal acts as the cathode which provides electrons to the water at the interface between SiNy and Al\textsubscript{x}Ga\textsubscript{1-x}N when the gate-to-drain diode is reversed biased. The corresponding reduction reaction for the water is:

\[ 2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^- . \] (3.2)

The electrons contribute to the total gate current. On the other hand, the Al\textsubscript{x}Ga\textsubscript{1-x}N layer acts as the anode and is decomposed and subsequently anodically oxidized in the presence of holes and hydroxyl ions (OH\textsuperscript{-}) as in the following reactions:

\[ 2\text{Al}_x\text{Ga}_{1-x}\text{N} + 6\text{h}^+ = 2x\text{Al}^{3+} + 2(1-x)\text{Ga}^{3+} + \text{N}_2 \uparrow \] (3.3)
And

\[ 2x\text{Al}^{3+} + 2(1-x)\text{Ga}^{3+} + 6\text{OH}^{-} = x\text{Al}_2\text{O}_3 + (1-x)\text{Ga}_2\text{O}_3 + 3\text{H}_2\text{O}. \]  \hspace{1cm} (3.4)

Figure 3-7. An electrochemical cell formed at the drain edge of the gate in AlGaN/GaN HEMTs under high OFF-state drain bias.

The decomposition of the Al\textsubscript{x}Ga\textsubscript{1-x}N (the GaN cap and the AlGaN barrier) causes the surface pitting that is observed in the SEM, AFM and TEM analyses. The subsequent formation of the aluminum and gallium oxides explains the origin of the high concentration of oxygen in the pitting area. Moreover, we find a high concentration of gallium in the gate metal region for the AlGaN/GaN HEMTs stressed in both humid and dry environments...
(including vacuum), while unstressed HEMTs showed no gallium in the gate metal region as shown in Figure 3-8. In addition, the gallium is found to be more concentrated at the drain edge of the gate than at the source edge of the gate as seen in Figure 3-9. The same phenomenon has been observed for aluminum (not shown). In the meantime, we can also find in Figure 3-8 that although there is Ga/Al out-diffusion into the gate metal, there is no gate metal out-diffusion into the GaN/AlGaN layers. This provides good evidence of the \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) decomposition, as the positive \( \text{Ga}^{3+} \) ions of equation (3.3) would migrate to the negatively biased gate metal along the electric field in the reverse-gate-bias condition. Another interesting feature we find in Figure 3-8 and Figure 3-9 is that the Ga atoms actually out-diffuse into the gate metal where the electric field should be close to zero. Since the room-temperature diffusivity of Ga in Au metal is as large as \( 7.9 \times 10^{-6} \text{ cm}^2/\text{s} \) [53]. Therefore the corresponding diffusion length \( \sqrt{Dt} \) of 1 s is around 28 \( \mu \text{m} \). It is not surprising that this out-diffusion process could occur given an injection source of unbounded \( \text{Ga}^{3+} \) ions at the gate edge.
Figure 3-8. TEM EDX mapping of gallium (Ga) and gold (Au) at the drain edge of the gate of AlGaN/GaN HEMTs unstressed (a) and stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V for 3000 s in water-saturated Ar (b) and in dry Ar (c).
Figure 3-9. TEM EDX mapping of gallium (Ga) concentration at the source (left half) and drain (right half) edge of the gate of AlGaN/GaN HEMTs unstressed (a) and stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V for 3000s in dry Ar (b) and in water-saturated Ar (c).

In summary, for the corrosion process to happen, it is necessary that:

1) Holes are available at the top III-Nitride surface at the gate edge during the high OFF-state drain bias condition.

2) Water from the ambient diffuses/permeates through the bulk SiN$_y$ passivation layer and reaches the III-Nitride surface.

The next two sections will discuss these two conditions in detail.
3.5 The Source of Holes

3.5.1 Photo-generated holes

It is widely accepted that holes are required for the decomposition and oxidation of GaN [54]. A good example is the photo-enhanced chemical (PEC) etching method where UV-generated holes in GaN assist in the formation of Ga$_2$O$_3$ in water, after which the oxides are subsequently dissolved in basic solutions [55][56]. The electrochemical reactions in the GaN PEC etching process are very similar to the proposed equation (3.2) and (3.3). In fact, UV light illumination is found in this work to accelerate the surface pitting in the OFF-state degradation of AlGaN/GaN HEMTs as well. This is demonstrated in the SEM image in Figure 3-10 (a) (after gate removal) in one of the AlGaN/GaN HEMTs that is stressed at a high drain OFF-state bias ($V_{gs} = -7$ V and $V_{ds} = 43$ V) for 3000 s in ambient air under UV light (254 nm) illumination. Compared to the SEM image in Figure 3-4 (a), when identical AlGaN/GaN HEMTs are stressed under the same bias and time conditions but in darkness, structural degradation such as seen in Figure 3-10 (a) is obviously accelerated. TEM images made before removal of the gate metal also show larger pits in the transistors that are stressed with UV light illumination in Figure 3-10 (b), than in the one stressed in darkness (Figure 3-5 (a)).

The above experimental evidence shows that holes indeed play an important role in the surface pitting phenomenon in OFF-state degradation. However, it does not explain where the holes are coming from when the sample is degraded in the dark. In principle, holes can be generated under high electric field by two mechanisms: i) impact ionization and/or, ii) direct or indirect inter-band tunneling. These two different scenarios are discussed and examined in the following two subsections.
ionization coefficient, which is exponentially proportional to the negative inverse of the electric field [57]. Therefore, most of the impact ionization occurs in the region with the maximum electric field ($E_{\text{max}}$), so equation (3.5) can be written as

$$j_{\text{ion}}^{\text{hole}} = \alpha \exp\left(-\frac{E_i}{E_{\text{max}}}\right) j_0 L_{\text{eff}},$$

(3.6)

where $\alpha$ is a constant coefficient, $E_i$ is a characteristic electric field for the impact ionization and $L_{\text{eff}}$ is the effective length of the high field region. For AlGaN and GaN, $E_i$ is around 34 MV/cm according to [57][60].

Figure 3-11. Schematics of the band diagram in the middle of the 14 nm AlGaN barrier along the lateral direction from source to drain at $V_{gs} = -7$ V and $V_{ds} = 43$ V. Gate electrons enter the high field region at 1 and obtain energy $\Delta E$ from the electric field at 2 where impact ionization is triggered when $\Delta E > E_g$ (a) and is not triggered when $\Delta E < E_g$ (b).
ionization coefficient, which is exponentially proportional to the negative inverse of the electric field [57]. Therefore, most of the impact ionization occurs in the region with the maximum electric field \( E_{\text{max}} \), so equation (3.5) can be written as

\[
    j_{\text{ion}} = \alpha \exp\left(-\frac{E_i}{E_{\text{max}}} \right) j_g L_{\text{eff}},
\]

where \( \alpha \) is a constant coefficient, \( E_i \) is a characteristic electric field for the impact ionization and \( L_{\text{eff}} \) is the effective length of the high field region. For AlGaN and GaN, \( E_i \) is around 34 MV/cm according to [57][60].

Figure 3-11. Schematics of the band diagram in the middle of the 14 nm AlGaN barrier along the lateral direction from source to drain at \( V_{gs} = -7 \) V and \( V_{ds} = 43 \) V. Gate electrons enter the high field region at 1 and obtain energy \( \Delta E \) from the electric field at 2 where impact ionization is triggered when \( \Delta E > E_g \) (a) and is not triggered when \( \Delta E < E_g \) (b).
In Figure 3-11 (a), we schematically illustrate the impact ionization process on the band diagram of the AlGaN layer. Electrons tunnel from the gate and enter the high field region at 1. They obtain energy $\Delta E$ from the electric field at 2 which is larger than the band gap of the AlGaN and thus cause impact ionization and electron-hole pair generation at 3. The holes drift toward the source and accumulate under the source side of the gate, which is away from the high field region. Some of these holes can be swept to the negatively biased gate electrode and contribute to the gate current [58]. However, the characteristic bell-shaped gate current curve for impact ionization has never been observed in GaN HEMTs in that the gate current is dominated by Schottky tunneling mechanism and therefore cannot be used as an indicator of impact ionization [15]. This makes the existence of the impact ionization hard to be experimentally tested. Another argument for impact ionization being unlikely to occur in GaN HEMTs is that the electrons injected from the gate might hop through defect-related traps in the AlGaN barrier and enter the high field region at 1 as shown in Figure 3-11 (b). From there, the electrons cannot get enough energy from the electric field to cause impact ionization.

Although the existence of hole current caused by the impact ionization in GaN HEMTs is still under debate, we will see in subsection 3.5.4 that the volume of surface pits provides a better way to quantify the hole current than the gate leakage current. Moreover, quantifying the relationship between the hole current and the electric field finally enables us to experimentally determine the source of holes in the electrochemical degradation of AlGaN/GaN HEMTs.

### 3.5.3 Inter-band Tunneling

Under a high electric field, electrons from the valence band in the AlGaN barrier could also directly tunnel through the barrier into the conduction band. This process leaves holes in the valence band that can migrate to the surface as illustrated in Figure 3-12 (a).

This direct inter-band tunneling would generally obey the Keldysh equation [61][62][63]:

\[
\text{Keldysh equation}
\]
\[ j_{\text{tunnel}} = CE^2 \exp(-\frac{E_t}{E}) , \]  

where \( j_{\text{tunnel}} \) is the tunneling current density, \( C \) is a constant, \( E \) is the electric field, and \( E_t \) is a characteristic electric field for direct tunneling in AlGaN and can be explicitly given by [61]:

\[ E_t = \frac{\pi}{2q\hbar} m_{\parallel}^{1/2} E_g^{3/2} , \]  

where \( m_{\parallel} \) is the reduced effective mass of electrons and holes in the direction of the electric field and \( E_g \) is the band gap. By using \( m_{\parallel} \approx 0.2 m_e \) [64], where \( m_e \) is the electron mass and \( E_g \approx 4.1 \) eV for Al\(_{0.28}\)Ga\(_{0.72}\)N in this study, we get \( E_t \approx 212 \) MV/cm, which is around 6 times larger than the characteristic field for impact ionization. It seems that the inter-band tunneling is much less likely to happen than the impact ionization due to a higher characteristic electric filed. However, this physical picture ignores a very important feature in AlGaN/GaN HEMTs, that is that the AlGaN layer is populated with traps [\]. In fact, trap-assisted tunneling has already been shown to be responsible for the large Schottky gate leakage current [65]. It is then likely that inter-band tunneling is also enhanced by defect-related traps in the AlGaN barrier as illustrated in Figure 3-12 (b), and therefore the characteristic electric field \( E_t \) could be significantly lowered in the real devices.
Figure 3-12. Schematics of the band diagram at the drain edge of the gate along the vertical direction from the GaN cap to the buffer layer, at $V_{gs} = -7$ V and $V_{ds} = 43$ V. Direct inter-band tunneling (a) and trap-assisted inter-band tunneling (b) in the AlGaN barrier.

3.5.4 Surface Pitting and Holes

The hole current density in the OFF-state that would be required to explain the structural degradation of AlGaN/GaN HEMTs can be estimated from equation (3.3), where the decomposition of one mole of AlGaN corresponds to 3 moles of holes. Therefore, to be able to explain the structural defects observed in GaN HEMTs, the average hole current density over the electrical stressing duration should be:

$$ \overline{j_{h}} \propto \frac{3VpN_Aq}{MAt} = \frac{3d\rho N_Aq}{Mt} \quad \text{(3.9)} $$

where $V$ is the volume of the surface pits, $\rho$ is the Al$_x$Ga$_{1-x}$N density, $M$ is the Al$_x$Ga$_{1-x}$N molar mass, $A$ is the pitting area, $t$ is the electrical stressing duration, $N_A$ is Avogadro's constant and $\overline{d}$ is the average depth of the pits.
For the purpose of providing experimental measurements of the average depth of the surface pits as a function of the electric field, six identical AlGaN/GaN HEMTs on another chip are stressed in ambient air for 1000 s at the same reverse gate bias ($V_{gs} = -7 \, \text{V}$) but at different drain bias from $V_{ds} = 3 \, \text{V}$ to $53 \, \text{V}$ with $10 \, \text{V}$ per step to make the $V_{dg}$ from $10 \, \text{V}$ to $60 \, \text{V}$. After stressing and recording of the electrical characteristics, the SiNy passivation and the gate metal of the samples are wet etched by the procedure described above to expose the surface around the gate. AFM surface analyses are then carried out and the average depth of the surface pits in each transistor is calculated by the scanning probe image processor (SPIP™) software in a $1 \, \mu\text{m} \times 0.1 \, \mu\text{m}$ region at the drain edge of the gate. Figure 3-13 below shows the top-view AFM images of the transistor surface with a $1 \, \mu\text{m} \times 1 \, \mu\text{m}$ gate area of devices stressed under different bias conditions. As we can see that the pit size and density at the drain edge of the gate (left line) increase with the drain-to-gate bias, but do not change at the source side of the gate (right line) due to the same gate-to-source bias applied to all of these transistors.

$V_{gs} = -7 \, \text{V}, \, V_{ds} = 3 \, \text{V}$  $V_{gs} = -7 \, \text{V}, \, V_{ds} = 13 \, \text{V}$
Figure 3-13. AFM top-view images of the surface morphology of the AlGaN/GaN HEMTs stressed at different bias conditions in ambient air for 3000 s. The left line in each image is the drain edge of the gate.
In order to convert the bias condition to electric field, the E-field near the gate is simulated using the 2-D device simulator Silvaco Atlas®. As expected, Figure 3-14 (a) shows that the maximum in the electric field coincides with the triple-line at the drain edge of the gate where the structural degradation occurs, under all the calculated bias conditions. The maximum electric field $E_{\text{max}}$ is then plotted with the average measured pit depth calculated from Figure 3-13 as a function of the drain-to-gate bias in Figure 3-14 (b).

Figure 3-14. Simulated total electric field as a function of lateral position in the AlGaN barrier (a). The values are averaged over the thickness of the AlGaN barrier in the vertical direction. Extracted maximum electric field at the drain edge of the gate and average pit depth measured as a function of the drain-to-gate bias (b).

$log(j_h/E_{\text{max}}^2)$ as a function of $1/E_{\text{max}}$ using the simulated values of $E_{\text{max}}$ and $j_h$ calculated from equation (3.9) is shown in Figure 3-15. It can be seen that $log(j_h/E_{\text{max}}^2)$ follows a linear trend with $1/E_{\text{max}}$ in agreement with equation (3.7), supporting our suggestion that hole-generation is caused by inter-band tunneling. The slope of the fitted line corresponds to the characteristic tunneling field in the AlGaN barrier which is around 7.7 MV/cm. This value of $E_t$ is much smaller than 212 MV/cm, the theoretical estimation above.
supporting the hypothesized scenario of trap-assisted inter-band tunneling illustrated in Figure 3-12 (b).

Figure 3-15. \( \log(\frac{j_h}{E_{\text{max}}^2}) \) (blue circles) and \( \log(\frac{j_h}{j_g}) \) (green triangles) as a function of \( 1/E_{\text{max}} \). The number of holes extracted from the volume of the pits seems to follow the inter-band tunneling model – left y axis and not the impact ionization model – right y axis.

At the same time, \( \log(\frac{j_h}{j_g}) \) as a function of \( 1/E_{\text{max}} \) is also plotted in Figure 3-15 by using the in-stress gate current averaged over the stress time \( j_g \) (as indicated in Figure 3-3) on a 50 \( \mu \)m x 0.25 \( \mu \)m gate area measured during the OFF-state electrical stressing for each transistor. As can be seen, the hole current needed to feed the growth of the pits is just a very small component of the total gate current. More importantly, \( \log(\frac{j_h}{j_g}) \) is an increasing function of \( 1/E_{\text{max}} \), which opposes equation (3.6) and indicates that the holes that contribute
to pitting cannot arise from impact ionization. Even though the theoretical estimations of the characteristic electric field for impact ionization to occur is much lower than for inter-band tunneling, it is most likely that the impact ionization is not responsible for the hole generation in OFF-state stress of AlGaN/GaN HEMTs.

Therefore, we conclude that the holes for the electrochemical reactions discussed in Section 3.6 are likely to arise through trap-assisted inter-band tunneling in the AlGaN barrier. However, to fully understand the mechanisms of the impact ionization and inter-band tunneling in AlGaN/GaN HEMTs, rigorous modeling and direct hole current measurements are still needed, which is out of the scope of this thesis.

3.6 The Source of Water

In addition to holes, the proposed electrochemical reaction mechanism requires a source of water. In ambient air, there exists a thin layer of adsorbed water on the surface of most solids [66]. Moreover, ambient water can diffuse or permeate through bulk solids with a rate defined as the water vapor transmission rate (WVTR). For a thick (> 100 nm) PECVD SiNy passivation layer, this rate is on the order of 0.01-0.1 g/m²/day [67][68]. In fact, the WVTR is an important limiting factor on the total electrochemical reaction described in equation (1) and can be estimated by the formation rate of the surface pits using the following formula:

\[
WVTR \approx \frac{3}{2} \frac{V \rho M_{H_2O}}{MAt}
\]  

(3.10)

where \( M_{H_2O} = 18 \) g/mol is the molar mass of water and the rest of the symbols are the same as in equation (3.9). A calculation based on equation (3.10) shows that the minimum WVTR needed to cause the observed density and size of the pits is around 0.05-0.1 g/m²/day, which matches well the typical value of the WVTR for PECVD SiNy [67][68].
With this rate, it takes only ~30 s to form a water layer at the interface between the SiNy passivation and the III-Nitride surface with a concentration of $1 \times 10^{13}$ cm$^{-2}$. As the water reaches the III-Nitride surface, reaction (3.1) occurs and the water molecules are consumed. For dry environment, the oxidation process will stop when all the water stored in the SiNy passivation layer are consumed. This explains well why we could still observe a small amount of surface pits in vacuum (Figure 3-4 (b)) and in dry Ar (Figure 3-6 (b)). On the other hand, for wet environment, the oxidation process will continuously occur due to the unlimited supply of water molecules from the atmosphere, and therefore the surface pits grow much larger (Figure 3-4 (a) and Figure 3-6 (a)).

3.7 Relationship between Structural and Electrical Degradation

Analyses on the drain current recorded in the experiment described in Section 3.3 have already showed that the drain current degradation is significantly suppressed in AlGaN/GaN HEMTs that were stressed in dry atmosphere (including vacuum) compared to HEMTs stressed in water-saturated atmosphere (including ambient air) for which the pits are large. Here we demonstrate the close relationship between drain current drop and the surface pits formation by using the time evolution measurements. Identical AlGaN/GaN HEMTs are stressed for different stress time from 1 ms to $10^4$ s at $V_{gs} = -7$ V and $V_{ds} = 43$ V in air and in vacuum respectively. Figure 3-16 below shows the time evolution of the surface morphology of the devices stressed in air. It can be clearly seen in Figure 3-17 that as the stress time increases, the drain current degradation (blue circles) follows the pit formation (red triangles) very well. The drain current collapse (green crosses) obtained by pulsed IV measurements with pulse width 250 ns also shows the same trend. It is therefore likely that the formation of the pits on the AlGaN surface impacts the drain current degradation [69]. One potential mechanism could be that the surface pits decreases the average thickness of the AlGaN barrier and thus decreases the average electron concentration in the channel, which leads to a higher access resistance and a lower drain current. In addition, as the oxidation is located at the gate edge and the area underneath the gate is not oxidized as shown in Figure 3-5, the $V_t$ would largely remain unchanged.
Figure 3-16. AFM top-view images of the surface morphology of the AlGaN/GaN HEMTs stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V in ambient air from 100 ms to 10000 s.

Figure 3-17. Drain current ($I_d$) degradation ratio (blue circles) defined as the after-stress $I_d$ divided by unstressed $I_d$ at $V_{ds} = 5$ V and $V_{gs} = 0$ V, $I_d$ collapse ratio (green crosses) defined as the after-stress pulsed $I_d$ divided by after-stress quasi-static $I_d$ at $V_{ds} = 5$ V and $V_{gs} = 0$ V, and the average pit depth as a function of stress time. The AlGaN/GaN HEMTs were stressed at $V_{gs} = -7$ V and $V_{ds} = 43$ V in ambient air (a) and in a vacuum of $1\times10^{-7}$ Torr (b).
On the other hand, as already shown in Figure 3-3, the gate current degrades well before any pit formation and does not vary much with stress time. It seems that the $I_g$ degradation might have a different origin altogether. This observation confirms some previous reports on the uncorrelated nature between gate current increase and output current drop [70][71][72]. One possible explanation, as suggested by Figures 3-8 and 3-9, is that the migration of gallium might lead to trap states at the interface of gate metal and III-Nitride layer, and thereby cause an increase in the gate leakage current. However, to fully understand this mass-transport process and its association with permanent gate current degradation, more work is needed in the future.

### 3.8 Conclusions

In conclusion, a mechanism involving water-assisted electrochemical reactions at the gate edge of GaN transistors has been proposed to explain the OFF-state structural degradation (surface pitting) in these devices. We show that water from the passivation layer surface and the atmosphere, as well as holes caused by trap-assisted inter-band tunneling in the AlGaN barrier are likely to play an essential role in forming the surface pits. Moreover, permanent drain current degradation has been explained by the reduction of the AlGaN barrier caused by surface pitting, while further investigation is still needed to fully understand the origin of the permanent gate current degradation.

The work of this Chapter has been partially published in [73].
Chapter 4 Impact of Moisture on Transient Degradation

4.1 Introduction and Motivation

For AlGaN/GaN HEMTs to show their full potential, reliability is one key as we have discussed in Chapter 2 and Chapter 3. As the devices are also targeted for power switching and microwave frequency applications, it is very important to control their transient degradations such as current collapse [36]. Current collapse, also known as dynamic on-resistance, is a decrease of the maximum drain current together with an increase in knee voltage and on-resistance when the devices are operated under pulsed conditions or large-signal microwave frequencies. In 2000, SiNₓ passivation was found to be effective in suppressing the current collapse and largely improving the output power density of AlGaN/GaN HEMTs [42]. Shortly after, the concept of the virtual gate was proposed to explain the mechanism of the current collapse observed in GaN-based transistors [39]. (Please refer to Chapter 1 for more details of the virtual gate model.) Nowadays, it is widely accepted that the current collapse phenomenon is the result of electrons from the gate being trapped at the AlGaN surface states and acting as a virtual gate to deplete the 2DEG channel and make the total charge neutral [39][74]. Although SiNₓ passivation is widely used to prevent current collapse, the exact mechanism by which SiNₓ passivation works is still not clear. In this Chapter, we will study the impact of different ambient gases and passivation materials on the current collapse of AlGaN/GaN HEMTs. The main goal of this Chapter is to provide a new insight on the possible explanations for the physical nature of the transient degradations in III-Nitride transistors. More rigorous and systematical experiments and theories will be elaborated in Chapter 5.

In Chapters 2 and 3, we have found that a water-assisted field-induced electrochemical reaction plays a significant role in device permanent degradations. Inspired by that, it is found in this Chapter that moisture or residual water molecules on device surface can also play a significant role in the DC-to-RF performance transient degradation of GaN-based HEMTs. Previously, an air ionization model was proposed [75] to explain the suppression of current collapse in vacuum, however there was no further discussion about the role of
moisture. Here, we present evidence that ionized water molecules or hydroxyl groups (OH⁻) on the device surface charge up the surface and form a virtual gate responsible of the current collapse and dynamic on-resistance. This finding may explain why SiNₓ, a hydrophobic material, is a good passivation to suppress transient degradations, while other hydrophilic materials such as SiO₂ are not. In fact, the use of fluorocarbon (Teflon®) C₄F₈ passivation has been shown to suppress the current collapse of AlGaN/GaN HEMTs as well as the SiNₓ passivation did, even when the Teflon passivation layer is not directly touching the AlGaN surface.

4.2 Device Structure

The devices studied in this work are fabricated on AlGaN/GaN heterostructures grown on sapphire substrates using metal organic chemical vapor deposition (MOCVD). The total top to bottom AlGaN/GaN structure is the following: a 4 nm unintentionally doped AlGaN layer, a 14 nm Si-doped AlGaN layer at a doping level of 3×10¹⁷ cm⁻³, a 5 nm unintentionally doped AlGaN layer, a 1.2 μm unintentionally doped GaN layer and a 0.7 μm Fe-dope GaN layer. The component of Al of all the AlGaN layers is around 0.25. AlGaN/GaN HEMTs are fabricated on these wafers using standard fabrication technology. Ohmic contacts are formed through Ti/Al/Ni/Au metallization and annealed at 870 °C in N₂ environment. A Ni/Au/Ni metal stack is used for the Schottky gate contact. The devices are tested without passivation, as well as with thin layers of SiO₂ and fluorocarbon passivation deposited by plasma enhanced chemical vapor deposition (PECVD). Before passivation deposition and electrical test, the devices are washed in Acetone and Isoproponol to remove organics, rinsed in deionized (DI) water and baked at 130°C for 5 minutes for dehydration. All the devices have identical geometries, with a gate length of 2 μm, a gate-to-source/drain distance of 1.5 μm, and a gate width of 2×75 μm. The device structure is schematically shown in Figure 4-1.
4.3 Measurement Setup

In order to investigate the impact of ambient moisture on the current collapse of AlGaN/GaN HEMTs, the relative humidity of ambient air has to be controlled. For this purpose, the experimental system shown schematically in Figure 4-2 is used. The AlGaN/GaN HEMTs are wire-bonded to a chip carrier and then mounted on the stage of an air-tight chamber where different gases can be flown through. The gases including ambient air, helium (He), oxygen (O₂), nitrogen (N₂) and carbon dioxide (CO₂) pass through one of the two different lines to make the chamber either dry or wet. In the dry gas line, two drying units from W. A. Hammond Drietite Co. are used to minimize the amount of moisture. These drying units dry the air to a dew point of -100°F at atmospheric pressure and room temperature, corresponding to a relative humidity (RH) ≈ 0.01%. In the wet gas line, the gases are flown through a deionized (DI) water bubbler and from there into the measurement chamber. Therefore, the RH in this case is close to 100%. The gas flow rate is set to 100 sccm by a mass flow controller. All the measurements are performed in darkness.
4.4 Experiments

First, the DC characteristics of a fresh device without passivation layer are measured in dry air (RH ≈ 0.01%) and ambient air (RH ≈ 40%) respectively. The chamber is kept open when we refer to ambient air condition. Then, pulsed I-V measurements are carried out on this device in both dry and ambient air. The drain voltage is swept from 0 V to 25 V, while the gate voltage is pulsed from -10 V to 0 V following a 100 Ω load line and a pulse width of 250 ns. The bias set up is schematically demonstrated in Figure 4-3.
The ON-state (at $V_{gs} = 0$ V) drain current measured in both dry and ambient air as a function of the drain voltage are shown in Figure 4-4 by black dash-dotted lines. No difference is observed between dry and ambient air under DC measurements. However, a large difference in the current level can be observed between the pulsed I-V measurements in dry (red solid line) and ambient air (blue dash line). While there is significant current collapse in ambient air, the current collapse is completely eliminated in dry air. In fact, under dry air condition, the drain current is larger under pulsed measurements than in DC mode due to the reduction of device self-heating. This is because the electron mobility in the 2DEG channel of AlGaN/GaN HEMTs decreases with increasing temperature. Therefore, longer time of self-heating in DC mode would cause higher temperature and lower drain current level than in pulsed mode. Moreover, the on-resistance of the device measured in dry air does not change from DC to pulsed measurements ($R_{on} = 4.7 \, \Omega \cdot \text{mm at } V_{ds} = 0.5 \, \text{V}$), while the on-resistance increased to $6.1 \, \Omega \cdot \text{mm at } V_{ds} = 0.5 \, \text{V}$ in the device exposed to ambient air (on inset of Figure 4-4).
Figure 4-4. DC and pulsed characteristics of AlGaN/GaN HEMTs without passivation in dry and ambient air. The pulse mode is operated with a 100 Ω load line and a pulse width 250 ns.

To confirm the impact of moisture on the device current collapse, the DC and pulsed characteristics of adjacent fresh unpassivated devices are measured in dry and wet (i.e. water-saturated gas at room temperature) helium (He) gas respectively. The results obtained are similar to the case of using dry and ambient air. Identical results are also obtained with the other main components of the ambient air including nitrogen (N₂), oxygen (O₂) and carbon dioxide (CO₂) gas in dry and wet conditions. This series of experiments demonstrates the dominant impact of water vapor on the transient degradations of AlGaN/GaN HEMTs, which has never been found in previous studies. In addition, the dry device transient behaviors can be recovered in minutes by placing the device degraded by moisture in a dry environment. This recoverable feature is most likely due to the adsorption and desorption dynamics of the surface water molecules. Actually, in Chapter 5, we will see more clearly that these water molecules adsorbed on the device surface are responsible for the widely observed current collapse and dynamic on-resistance in AlGaN/GaN HEMTs.
The change of drain current as a function of RF pulse width is shown in Figure 4-5. In dry helium gas, the RF drain current increases with the decrease of the pulse width due to the reduction in self-heating effect, which is explained before. On the other hand, in wet helium gas, the pulsed drain current followed an opposite trend, decreasing as the pulse width is reduced. This time dependence may be explained by a relaxation time associated with the process of ionization and deionization of surface water molecules and their electrochemical reactions on the semiconductor surface.

Based on the above findings, it is natural to consider the hydrophobicity of the surface materials as an important factor that can change the amount of adsorbed water molecules on the device surface and also change the device transient performance. In chemistry, hydrophobicity is the physical property of a type of molecules that is repelled from a mass of water. The surface of a lotus leaf is a good example of a hydrophobic surface that water is hard to attach. To test this hypothesis that hydrophobic passivation materials may reduce the
transient degradations of AlGaN/GaN HEMTs, some identical devices are coated with hydrophobic fluorocarbon (C₄F₈) materials which is deposited by PECVD at room temperature. The nominal thickness of the fluorocarbon passivation layer is around 15 nm. As shown in Figure 4-6 below, fluorocarbon-passivated devices do not show any current collapse and dynamic on-resistance even when tested in wet He gas (blue solid line). The use of this very thin layer of fluorocarbon passivation completely suppresses the transient degradations of AlGaN/GaN HEMTs in both dry and wet environment.

![Figure 4-6](image-url)

Figure 4-6. DC and pulsed characteristics in dry and wet helium atmosphere of AlGaN/GaN HEMTs before and after fluorocarbon passivation.

To further demonstrate that the effectiveness of the passivation on the current collapse is related to preventing the access of water molecules to the surface of the transistor, not to deactivating the surface states of the AlGaN layer, we deposit a thin layer of fluorocarbon on top of a thin layer of SiO₂ so that the fluorocarbon passivation is not directly in contact with the AlGaN surface. The SiO₂ layer is deposited by PECVD with a nominal thickness of 15 nm for a first batch of devices and of 30 nm for a second one. Then a 15 nm layer of C₄F₈ is
deposited on top of the SiO$_2$ dielectric in the first batch of devices. Devices passivated only with a 15 nm layer of C$_4$F$_8$ are also used as reference. DC and pulsed I-V measurements are performed in all the devices under dry and wet helium gas conditions. As can be seen in Figure 4-7, the porous and hydrophilic SiO$_2$ cannot suppress the current collapse in the GaN transistor. However, the deposition of a 15 nm layer of C$_4$F$_8$, no matter it is directly on the AlGaN surface or just on top of the 15 nm SiO$_2$ layer, completely eliminates the current collapse in the AlGaN/GaN HEMTs. The 30 nm SiO$_2$-passivated devices also show significant current collapse compared to the devices passivated with a stack of 15 nm C$_4$F$_8$ and 15 nm SiO$_2$ (30 nm in total). The reason of this comparison is to rule out the impact of passivation thickness on the transient behaviors so that the effectiveness of this thin layer of fluorocarbon on top of the SiO$_2$ layer is indeed due to the prevention from the surface water molecules not just because of the increase in the passivation thickness. In Chapter 5, we will explain in more detail why thicker passivation layers are more effective than thin layers on reducing the transient degradations of AlGaN/GaN HEMTs.

Figure 4-7. DC and pulsed characteristics in dry and wet helium atmospheres of AlGaN/GaN HEMTs with SiO$_2$ and fluorocarbon passivation.
4.5 Discussions

The current collapse phenomenon has been an important research topic of the GaN community for a long time. Many surface mechanisms have been proposed to explain it but no one provides solid evidence. According to the work presented in the previous sections, any hydrophilic surface exposed to atmosphere is coated almost immediately with a thin layer of water and will introduce current collapse [76]. For the passivation materials studied in this work, water contact angle measurements in Figure 4-8 show that the fluorocarbon surface is indeed hydrophobic with a contact angle of 110° (> 90°), while the Al0.25Ga0.75N and SiO₂ surface are both hydrophilic (< 90°) with contact angles of 74° and 40°, respectively. The water layer on the surface may trap electrons due to the lineup of the semiconductor Fermi level and the electrochemical potential of the surface reactions. This has already been observed on the SiO₂ surface in organic field-effect transistors [77], carbon nanotube field-effect transistors [78] and diamond surface [79]. We will show in Chapter 5 that water molecules on the III-Nitride surface act as surface trapping states that can trap electrons from the gate to cause transient degradations widely-observed in AlGaN/GaN HEMTs.

![Figure 4-8. Water contact angle measurements on C₄F₈-passivated, unpassivated, SiO₂-passivated AlGaN surface (from left to right).](image-url)
4.6 Conclusions

Air moisture has been found to play a very significant role in the current collapse and dynamic on-resistance of GaN-based HEMTs. The prevention of air moisture, either by measuring the devices in dry air or by coating the dielectric passivation with a thin layer of hydrophobic material such as fluorocarbon materials (Teflon), suppresses the transient degradation of the transistors. In addition, since the fluorocarbon material has much lower dielectric constant (~ 2) than silicon nitride (~ 8), it also significantly reduces the fringe capacitance added by the passivation layers, which allows higher operating frequencies. These advantages make the fluorocarbon passivation very attractive for both high power and high frequency applications of GaN-based transistors. The work in this Chapter has also inspired us to build a more complete and quantitative model in the next Chapter in order to fully understand the physics of the transient degradation in AlGaN/GaN HEMTs.

The work of this Chapter has been partially published in [80].
Chapter 5 Water Redox Couples as Surface Trapping States

5.1 Introduction and Motivation

Trapping effects have always been one of the notorious barriers in the development of the GaN semiconductors. The deleterious influences of the electronic traps set limits to most of the microwave power and high-voltage switching applications through changing the electrostatic profiles of the devices [2]. Trapped electrons form quasi-static charge distributions and act to restrict pulsed current drain characteristics and high-frequency power output [3]. In recent years, significant efforts have been directed to understand and suppress the trapping effects in AlGaN/GaN high electron mobility transistors (HEMTs) as an area of particular interest [4]. A variety of phenomena have been recognized as trapping behaviors, such as current collapse, dynamic on-resistance, frequency-dependent transconductance dispersion, gate- and drain-lag transients, pulsed I-V compression and microwave power slump [5]. These research activities and terminologies in literature actually inherit in many ways from the development of GaAs field-effect transistors (FETs) [6]. It is not surprising that many of the measurement techniques and well-established knowledge developed and obtained in the course of the investigation of the trapping effects in GaAs FETs can be directly applied to GaN HEMTs as well [7]. In fact, in terms of trapping effects, GaAs- and GaN-based transistors share the important characteristics that trapping centers residing at the surface and in the buffer layers are primarily responsible for the limiting effects on high-frequency power performance [8]. Buffer traps are associated with the drain-lag transients and disappear in devices with conductive buffer layers [9]. The more prominent surface trapping effects are linked with the gate-lag transients and suppressed in devices with passivation layers, especially with silicon nitride passivation that is utilized in GaAs FETs in 1990 [10] and in GaN HEMTs in 2000 [11]. Although today GaAs-based devices are already well-commercialized and GaN are moving towards full market insertion, a consensus regarding the origin of the traps, especially the identity of the surface traps and their trapping mechanisms remains lacking. Most of the literature on surface trapping effects in AlGaN/GaN HEMTs has focused on the electrical signature of traps and methodologies for trapping analysis [81], however, there is little information on the physical configuration of
these traps. The main goal of this work is to explain the origin of the surface traps and the corresponding surface trapping mechanisms in AlGaN/GaN HEMTs.

Surface traps can be categorized into two types: intrinsic and extrinsic. Intrinsic traps such as surface defects and dangling bonds reflect the intrinsic properties of the surface of the material. On the other hand, extrinsic traps are associated with ambient adsorbates and fabrication residues. Adsorbates coming from the ambient air are not commonly considered important sources of surface trapping in GaN-based HEMTs [39]. However, it is not uncommon that ambient adsorbates, especially water molecules from the environment, could act as charge traps and influence the current transients of a variety of devices [5-9]. For example, years of research in modern silicon metal oxide semiconductor field effect transistors (MOSFETs) have shown that water-related slow charge traps exist on silicon oxide (SiO₂) surfaces when exposed to ambient air and that these traps are not removable by exposure to vacuum at room temperature [82]. More recently, Chua et al. [77] have found electrochemical trapping of electrons by moisture-induced silanol (SiOH) groups on the surface of silicon oxides in organic semiconductors. Kim et al. [78] have demonstrated that hysteresis performance in single-walled carbon nanotube (SWNTs) field-effect transistors (FETs) is mainly caused by adsorbed water molecules in ambient air. Charkrapani et al. [79] identified the role of oxygen and the water redox couple in impacting the surface conductive behavior of H-terminated diamond in ambient air and later this mechanism was applied by Aguirre et al. [83] to explain trapping effects in SWNTs FETs.

In Chapter 4, we have showed that ambient moisture is an important source of drain current collapse in AlGaN/GaN HEMTs and that the hydrophobic and/or hydrophilic nature of the device surface could have a significant impact on the device’s transient performance [80]. In this Chapter, we will further show that the dominant origin of the surface trapping effects in AlGaN/GaN HEMTs is directly linked with water-related extrinsic electronic traps at the device surface.

In Section 5.2, we summarize the device structure and experimental setup used in this work. In Section 5.3, we show that the dynamics of the trapping transients and gate currents as a function of the annealing temperature are highly related to the dynamics of the surface water by using in-situ electrical characteristic analysis. The role of the SiNₓ passivation on
the trapping transient is also discussed in terms of its ability to block water molecules from the AlGaN surface. Moreover, in Section 5.4, we provide direct evidence of the dynamics of water molecules on the AlGaN surface through in-situ X-ray photoelectron spectroscopy (XPS) surface analysis. The electrochemical origin of the surface trapping mechanisms is proposed in Section 5.5.

5.2 Device Structure

The AlGaN/GaN HEMTs studied here are fabricated on AlGaN/GaN heterostructures grown on SiC substrates using metal organic chemical vapor deposition (MOCVD). The thickness of the AlGaN layer and the GaN buffer layer are 16 nm and 1.9 μm respectively. The Al component in the AlGaN layer is around 0.26. Standard fabrication technology is followed in the AlGaN/GaN HEMTs. The ohmic contacts are formed through Ti/Al/Ni/Au metallization and annealed at 870 °C in N₂ environment. A Ni/Au/Ni metal stack is used for the Schottky gate contact. The first batch of AlGaN/GaN HEMTs are unpassivated, while the second and third batch are passivated with a layer of SiNx deposited by plasma enhanced chemical vapor deposition (PECVD) with 20 nm and 200 nm thickness, respectively. All the HEMTs have identical geometries, with a gate length of 1.5 μm, a gate-to-source/drain distance of 1.5 μm, and a gate width of 2x75 μm. The device structure is schematically shown in Figure 5-1.
In order to study the impact of surface adsorbates on AlGaN/GaN HEMTs, it is important to control the environmental conditions in all the measurements. For this purpose, a vacuum chamber outfitted with four microprobes and a thermal chuck capable of reaching 500 °C is utilized. The chamber also incorporates two gas lines so that gases could be introduced into the chamber in a controlled manner. The real and schematic images of the experimental setup can be found in Figure 3-2 (a) and (b).

5.3 Analysis of the In-Situ Electrical Characteristics

5.3.1 Dynamics of Transient Characteristics

First, unpassivated AlGaN/GaN HEMTs are tested in a vacuum chamber at room temperature (22 °C) with a vacuum pressure of $10^{-6}$ Torr. A threshold voltage of $V_g = -2.5$ V, on-resistance of 7.3 $\Omega \times \text{mm}$ and I-V curves at different gate biases are recorded in quasi-static conditions. Pulsed I-V measurements are carried out with the drain voltage swept from 0 V to 15 V and with the gate voltage pulsed from -10 V to 0 V. The pulse width is 250 ns, and the period was 1 $\mu$s for a duty cycle of 25%. (For schematics of the pulsed I-V...
measurement, refer to Figure 4-3.) Under these conditions, the on-state drain current (at $V_g = 0$ V) recorded after the stress is dropped to nearly zero, indicating very significant trapping effects during the 750 ns OFF-state stress (at $V_g = -10$ V). The devices are then annealed without breaking vacuum at different temperatures from 50 °C to 300 °C. Annealing temperatures above 300 °C might cause Schottky gate degradation and are thus avoided. The devices are annealed at each temperature for one hour and then cooled down to room temperature without breaking vacuum to characterize the pulsed I-V performance. To eliminate the impact of cumulative periods of vacuum annealing on the measured devices, the chamber is open to ambient air after each step, re-pumped to a vacuum pressure of $10^{-6}$ Torr and a different identical unpassivated AlGaN/GaN HEMT on the same wafer is then annealed and studied. The annealing process is illustrated in Figure 5-2 below.

Figure 5-2. Schematic of the in-situ pulsed I-V measurements after vacuum of annealing at different temperature for one hour.
The DC and pulsed I-V curves for different annealing steps are shown in Figure 5-3. We find a critical annealing temperature around 200 °C at which the pulsed on-state drain current starts to significantly increase with simultaneous reduction in the drain current collapse, dynamic on-resistance and knee-voltage work-out. The maximum drain current collapse can be seen more clearly in the inset of Figure 5-3, where the current collapse percentage (the percentage change between the maximum drain current in quasi-static and pulse mode with respect to the quasi-static values) falls sharply from nearly 98% to around 20% after the unpassivated AlGaN/GaN HEMTs are annealed above 200 °C in vacuum. More interestingly, this phenomenon is reversible, which means all the figures of merit in pulse mode go immediately back to their initial values after the devices are re-exposed to ambient air. Additionally, after vacuum annealing we observe negligible change in the electrical characteristics in quasi-static mode, including the device threshold voltage. Therefore, we believe that the critical temperature of 200 °C does not cause intrinsic change in the devices, but rather triggers the thermal desorption of extrinsic water molecules from the device surface. It is in fact well known from silicon oxide surface chemistry that hydrogen-bonded water layers cannot be removed by pumping in vacuum at room temperature, even over extended periods of time, but can be desorbed by thermal annealing in vacuum and/or in dry environment at temperatures above 200 °C [82].

More insight into the role of surface water dynamics can be obtained from the study of the transistor on-resistance ($R_{on}$) as a function of annealing temperature (Figure 5-4). Two different surface water dynamics are observed in Figure 5-4. For temperatures below 100°C, the water adsorbed on the AlGaN surface gradually evaporates and the dynamic on-resistance of the unpassivated AlGaN/GaN HEMTs decreases due to the reduced surface charging states. For temperatures between 100 °C and 200 °C, the physically adsorbed water molecules have fully evaporated, however the thermal energy is not enough to activate the chemical desorption of a thin layer of hydrogen-bonded water layer from the surface [78]. When the annealing temperature exceeds 200 °C, the unstable hydrogen bonds of the surface water layers start to break and the remaining water molecules are removed from the surface by vacuum pumping. At that point, a sudden decrease in the concentration of surface trapping states happens, which causes a significant decrease in the dynamic on-resistance of the device. Above 250 °C the reduction of the on-resistance slows down and reaches the value of
the quasi-static on-resistance value after vacuum annealing at 300 °C. At this point there is therefore negligible surface charging states and/or water molecules at the surface.

![Graph showing drain-to-source current (Ids) as a function of drain-to-source voltage (Vds) measured at room temperature (RT) under quasi-static and pulse mode respectively, after annealing devices at different temperatures in a vacuum of 1×10^-6 Torr. The inset shows the current collapse percentage (measured at RT) as a function of the annealing temperature. Vgs = 0 V.](image)

Figure 5-3. The drain-to-source current (Ids) as a function of the drain-to-source voltage (Vds) measured at room temperature (RT) under quasi-static and pulse mode respectively, after annealing devices at different temperatures in a vacuum of 1×10^-6 Torr. The inset shows the current collapse percentage (measured at RT) as a function of the annealing temperature. Vgs = 0 V.
Figure 5-4. The on-resistance measured under quasi-static and pulse mode at RT as a function of the annealing temperature. The inset shows the I-V curves in the linear region of the devices annealed at different temperatures in a vacuum of $1 \times 10^{-6}$ Torr. $V_{gs} = 0$ V.

Furthermore, increasing the annealing time above the critical temperature from one hour to 48 hours further reduces the knee-voltage work-out and maximum drain current collapse as shown in Figure 5-5.
5.3.2 Dynamics of Gate Current

We also find that the critical temperature of 200 °C for the reduction of trapping transients also triggers the OFF-state gate current dynamics in quasi-static mode. The AlGaN/GaN HEMTs undergo similar annealing processes as described above and the OFF-state gate currents (at $V_{ds} = 7$ V, $V_{gs} = -10$ V) and the ON-state gate currents (at $V_{ds} = 7$ V, $V_{gs} = 0$ V) are measured in-situ at room temperature in vacuum. As shown in Figure 5-6, the OFF-state gate currents increase after the devices are annealed above 200 °C, while the ON-state gate currents largely stay at the same level.
It is worth mentioning that this process is also reversible. Whenever the devices are
exposed to ambient air, the gate currents immediately return to their initial level. Therefore,
we believe that this phenomenon is also attributed to the dynamics of the surface water.
Under OFF-state, and in the presence of surface water, the electrons from the gate are
trapped at the water molecules, extend the effective gate length and suppress the gate leakage
current. As the water layers are thermally removed in vacuum, the effective gate length
shrinks and the gate leakage under OFF-state thus accordingly increase. However, under ON-
state, the electrons from the gate are not trapped in the water molecules, therefore the gate
leakage current does not vary much.

Figure 5-6 The drain-to-source current (I_{ds}) as a function of the drain-to-source voltage (V_{ds})
measured at room temperature (RT) under quasi-static and pulse mode after annealing the
devices at 300 °C for 1 hour and 48 hour respectively.
5.3.3 Dynamics of Surface Water

To highlight the impact of moisture on the trapping transients of the AlGaN/GaN HEMTs, we exposed unpassivated devices to a four-step treatment. The devices are first measured as described above in vacuum, showing large dynamic on-resistance and current collapse. Second, they are annealed at 300 °C for 48 hours, cooled down to room temperature and measured in-situ again in vacuum. The dynamic on-resistance disappears and the current collapse ratio drops to around 20%. Third, dry air (with humidity less than 1%) is introduced to the chamber to break the vacuum and the transient characteristics of the devices are found to stay at the same low level. Finally, the chamber is opened and the devices are exposed to ambient air. Almost immediately, the dynamic on-resistance and the current collapse surge to high values. This phenomenon is summarized in Figure 5-7. Clearly, environmental moisture and surface water dynamics play a key role here. The most probable explanation for the behavior of the transient dynamics observed appears to be related to the adsorption and desorption of water molecules on the AlGaN surface. The adsorbed surface water on the unpassivated AlGaN/GaN HEMTs, when exposed to ambient air, could not be removed by evacuating the chamber out at room temperature but could be largely removed from the surface by heating to 300 °C. The critical decrease in surface trapping centers resulting from the removal of surface water remains in devices exposed to environments with low humidity levels. However, as soon as the device is re-exposed to ambient air, the polar nature of AlGaN renders the surface hydrophilic (with a water contact angle of 74° [84]) leading to re-adsorption of the water molecules that contribute to the surface trapping states.
The four-step environmental treatment on the AlGaN/GaN HEMTs shows that the dynamics of the on-resistance and current collapse are highly correlated with the dynamics of surface water adsorption/desorption.

In summary, we find water molecules act as surface trapping states in unpassivated AlGaN/GaN HEMTs. For passivated devices, especially SiN$_x$-passivated devices, we will show a close relationship between the surface water dynamics and the device passivation in the following subsection.

### 5.4 Impact of Silicon Nitride Passivation

Silicon nitride (SiN$_x$) passivation was first introduced in the early of 90s to suppress trapping effects in GaAs FETs [85]. More recently, it was likewise applied to AlGaN/GaN HEMTs leading to a major improvement in the pulsed I-V characteristics and microwave power performance of these devices [86]. Although it is believed that the SiN$_x$ passivation prevents surface trapping by passivating surface states and blocking the injection of electrons
from the gate [86][87], the details of this mechanism remain unclear. In this section, we investigate the origin of the impact of SiN_x passivation on surface trapping effects in terms of the surface water dynamics.

Second and third batches of AlGaN/GaN HEMTs were passivated by PECVD deposition of 20 nm and 200 nm thick SiN_x films, respectively. The SiN_x deposition was operated under a base pressure of 1x10^{-5} Torr and at 300 °C. These devices were then analyzed in vacuum by pulsed I-V measurements as described above, vacuum annealed at 300 °C for extended periods of time to remove surface water molecules, and measured in-situ again after cooling down to room temperature. The I-V curves of the devices in quasi-static and pulse mode are compared in Figure 5-8. There are three important features that can be observed:

1) The maximum ON-state (V_g = 0 V) drain current in quasi-static mode shows a steady increase as the passivation layer becomes thicker. In fact, this increase of the drain current is also associated with a threshold voltage shift towards more negative gate bias after the deposition of the SiN_x (data not shown). These phenomena in quasi-static mode were consistently observed in previous studies as well [88].

2) Before annealing, the pulsed drain current (blue circles) shows clear differences between unpassivated and passivated devices and, also, within the passivated devices. Significant dynamic on-resistance is observed for the unpassivated (Figure 5-8 (a)) and the 20 nm SiN_x-passivated devices (Figure 5-8 (b)), but not for the devices with 200 nm SiN_x passivation (Figure 5-8 (c)).

3) After annealing in vacuum, all pulsed drain currents reach a level around 10% below the quasi-static value (black line). No dynamic on-resistance is observed in any of the unpassivated and passivated devices.

Based on the above facts, we can propose a new hypothesis to explain the role of SiN_x passivation on the suppression of surface trapping effects. First, since no change is observed in the quasi-static characteristics of each individual device before and after vacuum annealing, the influence of the SiN_x passivation on the 2DEG concentration thus acts to amplify the drain current and can be normalized for simplicity. Second, it is obvious that the three types of devices exhibit nearly the same figures of merit in pulse mode after vacuum annealing.
More importantly, the thick SiNₓ passivation layer (200 nm) has the same effect on reducing surface trapping as vacuum annealing. It is therefore tempting to attribute the origin of the impact of SiNₓ passivation on transient performance of AlGaN/GaN HEMTs to the same mechanism of surface water dynamics proposed in the previous section. However, before we can make a firm conclusion of this relationship, a few points need to be clarified:

1) The thickness of the SiNₓ passivation layer plays a role in the transient performance of AlGaN/GaN HEMTs in that there are trapping states located at the SiNₓ surface. The trapped electrons on the SiNₓ surface form a virtual gate just as on the AlGaN surface in unpassivated HEMTs [87]. However, the thickness of the SiNₓ layer changes the distance between the gate electrode and the 2DEG channel, while the side walls around the gate also possibly hinder electron injection. As a result, the thicker the passivation layer, the less observable are surface trapping effects.

2) The trapping states on SiNₓ surface can be reduced by vacuum annealing just as early observations on AlGaN surface.

3) The interfacial water-related species between AlGaN and SiNₓ layers should be largely removed by NH₃ and SiH₄ at 300 °C in vacuum during the normal silicon nitride PECVD process, otherwise there exist significant discrepancy of the trapping transients between the 200 nm SiNₓ-passivated AlGaN HEMTs before annealing (blue circles of Figure 5-8 (c)) and the unpassivated AlGaN HEMTS after annealing (red rectangles of Figure 5-8 (a)), which is not observable.

Through the discussion above, the most possible scenarios experienced by the three types of AlGaN/GaN HEMTs are schematically demonstrated in the insets of Figure 6. Before annealing treatment, there are inevitable adsorbed water layers on unpassivated AlGaN and SiNₓ surfaces in ambient air due to the hydrophilic nature of these materials [84]. The adsorbed water molecules act as surface trapping states and capture electrons injected from the gate metal under reverse gate bias stress. The trapped electrons on the surface form a second gate, deplete the channel and cause the observed trapping transients (on-resistance increase and current collapse). After vacuum annealing above the critical temperature over extended periods of time, most of the water molecules are desorbed from the AlGaN and/or
SiN$_x$ surfaces and the surface trapping effects are suppressed by the reduction in the number of surface trapping states.

Figure 5-8. I-V curves and surface water dynamics of unpassivated AlGaN/GaN HEMTs a), AlGaN/GaN HEMTs passivated with 20 nm SiN b) and AlGaN/GaN HEMTs passivated with 200 nm SiN c) measured at room temperature under quasi-static and pulse mode before and after vacuum annealing at 300 °C.
5.5 In-situ XPS Analysis

*In-situ* X-ray photoelectron spectroscopy (XPS) surface analysis was applied to the AlGaN surface from the first batch of unpassivated AlGaN/GaN HEMTs to look at the signature of water-related surface states (hydroxyl groups) at room temperature. The O 1s core level of interest is scanned at high resolution and a survey scan is also conducted for surface configurations with binding energies between 0 and 1200 eV. The reported binding energies of the O 1s core level in AlN and GaN range from 530.7 eV to 532.5 eV [89]. The relatively broad spectrum of the O 1s core level is typically due to the convolution of two peaks [90]. The lower peak, with binding energy ranging from 530.7 to 531.5 eV, is assigned to O$_2^-$ species (oxides) while the higher peak, with binding energy ranging from 532.0 to 532.3 eV, is assigned to OH$^-$ species (hydroxides) [89]. By splitting the broad O 1s spectrum into O$_2^-$ and OH$^-$ peaks within the corresponding energy levels, we find that the oxygen coverage at the AlGaN surface in vacuum before annealing treatment is initially composed of almost half oxides and half hydroxyls groups as shown Figure 5-9 (a).

![Figure 5-9](image)

Figure 5-9. *In-situ* XPS analysis of the O 1s spectrum on the fresh AlGaN surface before (a) and after (b) vacuum annealing at 300 °C. The dashed lines show the peak shift of the O 1s core level. The measurements are conducted at room temperature.
Additionally, the ratio between the atomic concentration of O 1s and Ga/Al 2p at the surface is 2.10, which combined with the above O$^{2-}$ and OH$^-$ percentage ratios, leads to an atomic configuration at the AlGaN surface where there is roughly 1.08 O$^{2-}$ and 1.01 OH$^-$-related species per Ga/Al surface site (the upper red circle in Figure 5-10).

The sample is then annealed in vacuum of $10^{-6}$ Torr at 300 °C for one hour, cooled to room temperature and studied by XPS in-situ (i.e. without breaking vacuum). A peak shift towards the lower binding energy level of the O 1s is observed (from 531.4 eV to 531.1 eV as indicated with the dashed line in Figure 5-9). The deconvolution of the O 1s spectrum demonstrates that this time the OH related species is significantly reduced to ~16%, by contrast the O$^{2-}$ related species rises to ~84% of the total surface oxygen concentration as shown in Figure 5-9 (b). Similarly, atomic concentration ratio analysis shows that the O : Ga/Al ratio has decreased to 1.33 and thus the O$^{2-}$ : Ga/Al ratio is 1.12 and the OH$^-$ : Ga/Al is 0.21 (the lower red circle in Figure 5-10).

![Figure 5-10. The concentration of surface hydroxyl groups (OH$^-$) and oxides (O$^{2-}$) obtained by in-situ XPS on AlGaN surface before and after vacuum annealing at 300 °C. The measurements were conducted at room temperature.](image-url)
It is therefore clear that the vacuum annealing process causes desorption of the surface hydroxyl groups while the surface oxides remain largely intact. The reduction of the OH⁻ concentration after annealing treatment is likely caused by the thermally-activated breakage of unstable O-H bonds. As also suggested by Bermudez et al. [91], chemisorbed water forms OH⁻ on clean Ga-polar GaN (0001) surfaces which could be decomposed upon annealing at ~200 °C, as confirmed by synchrotron ultraviolet photoemission spectroscopy (UPS) studies.

The proposed link between hydroxyl groups on the AlGaN surface and air moisture has been extensively studied for other semiconductor systems. For example, in the case of Si transistors, it is well known that surface siloxanes react with water and revert to Si-OH when exposed to ambient air [92]. More importantly, as Chua et al. demonstrated in [93], the electrochemical OH electron-trapping mechanism on the silicon oxide surfaces depends on a redox couple between surface hydroxyl groups and hydrogen gas. For diamond and carbon nanotube surface trapping mechanisms, Chakrapani et al. [94] and Aguirre et al. [95] assigned the oxygen/water redox couple to the electron trapping centers. In the following section, we examine these two electrochemical reactions in terms of their electrochemical potentials and suggest that the H₂O/H₂ redox couple is likely to play a key role in the surface trapping in AlGaN/GaN HEMTs.

5.6 Hypothesis for the origin of current collapse in GaN-based transistors

Water in equilibrium with ambient air could contribute to formation of slow electron traps via two electrochemical redox couples involving oxygen and hydrogen respectively [96].

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^- \quad (5-1) \]

\[ 2\text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \quad (5-2) \]
The electrochemical potentials, $\mu_{e1}$ and $\mu_{e2}$, of these two redox reactions are determined by the Nernst equation.

\[
\mu_{e1}(eV) = \mu_0 - eE_1 - \frac{0.05916}{4}[4pOH + \log_{10}(pO_2)]
\]  \hspace{1cm} (5-3)

\[
\mu_{e2}(eV) = \mu_0 - eE_2 - \frac{0.05916}{2}[2pOH - \log_{10}(pH_2)]
\]  \hspace{1cm} (5-4)

$\mu_{e1}$ is for equation (5-1) and $\mu_{e2}$ is for equation (5-2). $\mu_0$ here is the electrochemical potential of electrons at the standard hydrogen electrode (SHE) referred to the vacuum level and is -4.44 eV [96]. The standard reduction potential at 298K and 1 atm for equation (5-1), $E_1$, is +0.401 V and for equation (5-2), $E_2$ is -0.828 V relative to SHE. The partial pressure of oxygen gas and hydrogen gas in atmospheric conditions is 0.21 bar and 5.5x10^{-4} mbar respectively [97]. Therefore subtracting equation (5-3) from (5-4), we obtain:

\[
\mu_{e2} - \mu_{e1} = 1.03(eV)
\]  \hspace{1cm} (5-5)

The energy gap between these two levels is therefore around 1 eV [98]. The thin water film acts as an interfacial layer between the metal gate and the AlGaN surface around the gate edge. In equilibrium, the Fermi energy of the system should be flat. If we assume the reaction rates or the electron transfer rates of equation (1) and (2) are only a function of the energy difference between the electrochemical potentials and the Fermi energy, then in equilibrium the rates are balanced and the Fermi energy should be located in the middle of the energy gap between these two water redox levels. Therefore, as schematically shown in
Figure 5-11 and Figure 5-12, the $\text{H}_2\text{O}/\text{H}_2$ redox couple forms a surface trapping state with an energy level around 0.5 eV above the Fermi level of the AlGaN/GaN HEMTs in equilibrium, which is also equivalent to around 0.5-0.6 eV below the AlGaN conduction band if we assume the Schottky barrier height is 1.0-1.1 eV [99]. This 0.5 eV energy difference is consistent with the activation energy that has been widely observed for the surface trapping states in AlGaN/GaN HEMTs [100], which makes water molecules important candidates to explain the origin of electron trapping states on III-Nitride surface.

Figure 5-11. Band diagram of AlGaN/GaN HEMTs in equilibrium. The Fermi level (dashed line) is located midway between the water redox couples.

Adsorbates, especially water-related chemical groups on AlGaN surface, can have a major impact on the electrical performance of GaN-based semiconducting devices. For example, if the concentration of Ga/Al atoms at the AlGaN surface is around $1\times10^{15}$ cm$^2$, a one-percent monolayer coverage of water or hydroxyl groups on the AlGaN surface could trap $10^{13}$ cm$^2$ electrons on the surface based on the redox reaction in equation (2). This amount of charge would deplete the whole channel and cause major current collapse and dynamic on-resistance given that the sheet carrier concentration in AlGaN/GaN HEMTs is
typically on the order of $1 \times 10^{13} \text{ cm}^{-2}$. The impact of surface adsorbates on the current collapse of devices is even true in passivated devices due to the non-zero water vapor transmission rate (WVTR) for most solid materials. For example, moisture penetrates 100-200 nm PECVD SiNx with a rate ranging from 0.01 g/m$^2$/day to 0.1 g/m$^2$/day [20-21]. With this rate, it takes only 26 s to form a water layer at the interface between the SiNx passivation and the GaN surface with a concentration of $1 \times 10^{13} \text{ cm}^{-2}$ (which is $3 \times 10^{-6} \text{ g/m}^2$). In real devices, the WVTR of the SiNx may vary widely due to the quality of the passivation, the humidity, the temperature, or the electric field in the dielectric, however, even if the WVTR can be reduced by 1000 times, it still takes less than 8 hours for water molecules to have a significant impact on the electrical performance of the III-Nitride devices.

![Figure 5-12. H$_2$O adsorption on AlGaN surface in ambient air at room temperature. The O-H bonds trap electrons from the gate.](image)

### 5.7 Conclusions

In summary, in this Chapter we propose the water-related redox origin of surface trapping states in AlGaN/GaN HEMTs. The supportive evidence includes:

1) In-situ pulsed I-V analysis of unpassivated AlGaN/GaN HEMTs annealed in high vacuum above a critical temperature around 200 °C show a dramatic
improvement in device transient performance, including the disappearance of the
dynamic on-resistance and significant decrease in drain current collapse. This
critical temperature ~ 200 °C is linked with the desorption process of surface
water molecules.

2) By switching the operating environment from dry air to ambient air, we find that
the dynamics of drain current collapse and on-resistance are identical to the
dynamics of surface water adsorption/desorption. Moisture in the air is therefore
largely responsible for the observed trapping effects.

3) In the framework of the proposed water-related trapping mechanism, the role of
the silicon nitride passivation in the transient performance of AlGaN/GaN
HEMTs is well explained as a barrier to moisture. The high-temperature
deposition processes of SiN also helps to remove water from the AlGaN surface.
Meanwhile, hydrophobic passivation materials with low dielectric constant such
as Teflon have also shows very promising results in eliminating current collapse
and trapping issues [84].

4) In-situ XPS analysis of AlGaN surfaces before and after annealing provides direct
evidence of the existence of water-related surface hydroxyl groups and the
reduction of OH− concentrations following vacuum annealing treatment above the
critical temperature which was directly connected to the reduction of surface
trapping states.

5) An electrochemical electron trapping mechanism related to the H₂O/H₂ redox
couple was proposed to further support the existence of water-related surface
trapping states on AlGaN surfaces. The electrochemical potential of the redox
reaction forms a surface state above the Fermi level with activation energy of 0.5
eV, consistent with the widely accepted value of the activation energy in current
collapse.

6) One percent monolayer coverage of water or OH− groups on the III-N surface
could have significant impact on the electrical performance of AlGaN/GaN
HEMTs. This small amount of water can be rapidly formed due to the non-zero
water vapor transmission rate (WVTR) of the passivation materials such as
PECVD SiNx.
The above six observations suggest that water-related redox couples play a significant role in the physical origin of the surface trapping states both in unpassivated and passivated AlGaN/GaN HEMTs. Future passivation technology should be oriented to prevent water adsorption and diffusion for better device performance.
Chapter 6 Summary and Future Work

6.1 Summary

To summarize, this thesis studies two major challenges in the field of AlGaN/GaN high electron mobility transistor reliability.

The first challenge is to understand the mechanisms of the permanent degradations in AlGaN/GaN HEMTs, including structural degradation such as surface pitting and electrical degradations such as drain current decrease and gate leakage current increase. By carefully controlling the stress environment, moisture in air is found to be a previously unrecognized but significant cause of the structural degradation in III-Nitride transistors. Based on that finding, a water-assisted electrochemical model is quantitatively established for the first time to clearly explain the whole degradation process occurred on the III-Nitride surface during the high drain bias electrical stress. The proposed hypothesis is strongly supported by direct experimental evidence. Moreover, the permanent drain current decrease is found to be highly correlated with surface pitting, while the gate leakage current increase is not. The first observation of gallium and aluminum out-diffusion into the gate metal not only supports the electrochemical reactions occurred at the gate edge, but also suggests a possible gate leakage path created by the gallium defect states at the gate edge that causes the gate current increase.

The second challenge is to understand the mechanisms of transient degradation in AlGaN/GaN HEMTs such as current collapse and dynamic on-resistance. Water molecules, again, are found to be a previously ignored but important factor for the transient degradation in III-Nitride transistors. In fact, water molecules adsorbed on the device surface form surface trapping states that can trap electrons from the gate under reverse gate bias and cause current collapse and on-resistance increase through the virtual gate model. Direct experimental evidence of the surface water redox states has been found by in-situ pulsed I-V measurements and in-situ XPS analyses. A critical temperature of 200 °C has been recognized to trigger the desorption process of the surface water on the semiconductor surface and to improve the transient behaviors of unpassivated AlGaN/GaN HEMTs. Moreover, the mechanism by which SiN passivation can suppress the current collapse of
AlGaN/GaN HEMTs but not SiO₂ passivation has finally been well understood by the proposed water-related surface trapping model. SiN materials are much better water barriers and more hydrophobic than SiO₂ materials, and therefore reduce the water absorption on the surface. Based on this finding, fluorocarbon (i.e. Teflon) materials have been used as passivation dielectrics and they were found to be excellent in suppressing any transient degradation in AlGaN/GaN HEMTs, due to their smallest surface energy and high hydrophobicity.

The above findings create a new direction in understanding the degradation mechanisms in GaN-based transistors and provide a solid base for further improvement on GaN reliability. These advances will hopefully bring the GaN technology to a more mature level and wider commercialization.

6.2 Future Work

Building upon the work described in this thesis, some future research directions are suggested below.

6.2.1 Building a comprehensive model for permanent gate current degradation

Critical gate voltage and permanent gate current increase have been systematically studied by J. Joh, et al. recently [23] and a hypothesis related to the inverse piezoelectric effect in the III-Nitride layer has been proposed as one of the possible mechanisms.

As we suggest in Chapter 3 that gate current permanent increase might also be linked with the gallium out-diffusion into the gate metal at the gate edge. This out-diffusion process is very likely to locally decrease the Schottky barrier of the III-Nitride surface and therefore create a gate leakage path to increase the gate current. To better understanding this mode of gate degradation, it is suggested to simulate or theoretically model how the lowering of the Schottky barrier increases the tunneling of the leakage current. Moreover, future work of this
part could be focused on studying the impact of different gate metals or gate oxides on preventing the out-diffusion of gallium under high bias conditions.

This comprehensive model should also include the temperature dependencies of the gate current degradation, the time dependencies as characterized in lifetime tests and the statistics (different vendors, different device structures, different fabrication processes, etc.). The ultimate goal is to build a quantitative model that can explain, predict and prevent permanent gate current degradations in GaN transistors.

6.2.2 Improving the passivation technology

As we have demonstrated in Chapter 4, Teflon passivation on AlGaN/GaN HEMTs could excellently suppress current collapse and dynamic on-resistance without even touching the AlGaN surface. However, this technology is still not very mature, partly because the Teflon material in this study is coated on the device at room temperature. This low temperature technology, in fact, cannot fully remove the surface water on the device surface (as we show in Chapter 5 that the temperature should be critically above 200 °C). Therefore, there might still be a thin layer of water between the device surface and the Teflon passivation layer, which makes the passivation not well attached to the semiconductor surface and more importantly unable to suppress transient degradations.

In the future work, it is suggested that during the passivation deposition step, the devices are vacuum annealed above 200 °C at the first place and then in-situ deposited by Teflon or other hydrophobic materials at their suitable coating temperatures. The two key steps in this process worth to be emphasized: 1. the devices should be vacuum annealed above 200 °C in order to fully remove the surface water; 2. if the optimized coating temperature of the chosen hydrophobic materials is below 200 °C, it is very important to cool down the devices without breaking the vacuum. This is to ensure that water molecules are not re-adsorbed on the device surface. Surely, this new process may involve refitting or even re-designing of the deposition system in the future work.
References


