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reason why such heterostructures are suitable candidates for usage as high power and high frequency devices such as high electron mobility transistors (HEMTs).1,2 Due to the intrinsic polarization field in c-plane AlGaN/GaN structures, the 2DEG channel is situated at the hetero-interface; however, the origin of the electrons for this channel is still in dis-
cussion: Ibbetson et al.3 first introduced the generally accepted idea of electrons arising from donor-like surface states at the AlGaN surface. Specifically, the control and modification of surface states, i.e., equal to the interface states in metal-insulator-semiconductor (MIS) HEMT devices, is a significant issue to allow normally off applications and reliable device performance. Moreover, the threshold voltage drifts that are obtained from forward gate-bias stress measurements4,5 are often linked to either surface/interface states or to defect states in the dielectric layer which is pas-
sivating the surface.6,7 Even though a few suggestions exist on the general properties of the III-N surface,8–10 the atomis-
tic view of the surface, the origin of the 2DEG, and the inter-
action with defects in the adjacent dielectric are still largely unknown. Oxygen, for instance, is discussed to play a major role in surfaces-state formation.11 Hence, a chemical surface modification attempting to reduce superficial oxygen (adsor-
bates) and to modify the chemical surface structure has been investigated by chemical cleaning as in Refs. 12–14 or ther-
ally treating15 the III-N surface. Other attempts include the exposure of those surfaces to plasmas16,17 or generally a dielectric deposition.18–20 Nevertheless, the oxygen surface-state modification fails because of insufficient oxygen removal from the heterostructure. Besides oxygen, other adsorbates are also suggested to play a role in electrical device behaviour.21–24 Sulphur atoms at the III-V surface faces after a chlorine-based clean over other cleans is not observed. More promising is such a surface chlorination of GaN surfaces for ultraviolet (UV) detector applications: it reduces the measurable surface state density.25 The halogen chlorine shares its great affinity with III-N surfaces with fluorine.25 In contrast to chlorine, fluorine termination is found to significantly change the electrical device behaviour of the AlGaN/GaN HEMT devices.24,26 Either fluorine is implanted27,28 as an ion into the AlGaN barrier, which induces a positive shift of the threshold voltage towards normally off behaviour, or the AlGaN surface is fluorinated by chemical interaction of F with the surface atoms.24,26 In the latter case, it is shown that a modification of the device behaviour by the presence of a new and dominant surface donor state is
induced. This likely modification of the “native” donor states is established by remote nitrogen trifluoride (NF3) or tetrafluoromethane (CF4) plasma processes.29

In this paper, we describe the detailed method in order to achieve this surface modification of the III-N device. We discuss the physical-chemical aspects of the AlGaN surface termination with fluorine as well as its application in combination with a silicon nitride (Si3N4) surface passivation layer. Moreover, we suggest how this surface modification can be achieved by a remote fluorine-based plasma and clearly differ from implanted fluorine using a plasma.

II. EXPERIMENTAL

20 nm Al0.22Ga0.78N on GaN (0001) on Si (111) samples is grown following a state-of-the-art metal-organic chemical-vapour-deposition process. The samples are subsequently cleaned with 0.5% aqu. hydrochloric acid (HCl). The reference samples (Ref.) did not see any surface treatment except the HCl based clean. For surface fluorination, the AlGaN samples are processed in a remote fluorine-based (NF3 or CF4) inductively coupled plasma (ICP) on a Mattson Aspen II (in the following referred to as “remote-ICP-F”) with the following parameters at 13.56 MHz: 900 W, 250 sccm N2, 800 sccm CF4 at 0.9 torr for 90 s or 900 W, 200 sccm N2, 500 sccm NF3 at 0.9 torr for 90 s. This process is compared to a Si3N4-based direct transformer coupled plasma (TCP) on a LAM TCP with the minimum bias of −60 V (referred to as “direct TCP-F”), similar to Ref. 27.

For comparison, the sample surfaces are also treated with the remote ICP oxygen (O2) plasma (performed on the same Mattson Aspen II) instead of fluorination. To understand the stability of the fluorination, some already fluorinated surfaces are subsequently treated with the remote ICP-O2 plasma. Additionally, gas mixtures of NF3/O2 and CF4/O2 are investigated, resulting in no difference from the solely CF4 or NF3 plasma in Auger electron spectroscopy or electrical analysis.

The surface analysis after each process step is performed by Auger electron spectroscopy (AES) on a Physical Electronics PHI-4700 at 5000 eV and 2 nA. Additional X-ray photoelectron spectroscopy (XPS) is carried out on a PHI Quantum 2000 with monochromatic Al-Kα (1486 eV) at 45°. For detailed F1s, Ga3d, and Al2p peak analysis, the pass energy with 0.1 eV steps and an averaged value from 500 spectra are monitored. Chemical shifts of Ga binding energies are taken from reference.30

To investigate the stability of the surface fluorination over time, the samples are stored for up to 180 h in a clean-room atmosphere and analysed by AES and contact-angle analysis. For contact-angle measurements, 10 µl of dideutero-methane after 15 s at 21.5 ± 0.3°C is used.31 Apolar solvents such as dideutero-methane are shown to deliver more accurate results on the strongly hydrophilic polar c-plane AlGaN surfaces. To understand the reversibility and chemical stability of the fluorination, the samples are cleaned with 0.5% aqu. HCl or 0.5% aqu. hydrofluoric acid (HF) after their plasma treatments and again analysed by AES, contact-angle, and electrical measurements. The thermal stability of the fluorine termination is investigated by effusion measurements: the gaseous species with different masses are detected using a Hiden Halo RGA spectrometer. Therefore, 1.5 cm × 1.5 cm samples are loaded onto a heating plate, and a temperature ramp of 5.33 K min−1 up to 1000°C is applied after a base pressure of less than 1 × 10−8 mbar is reached. At 1000°C, the temperature was fixed for 1 h to allow the probe to fully degas and analyse possible ongoing mass effusion at high temperatures. In this case, the decomposition of GaN is observed.

For electrical analysis of the state-of-the-art MIS-HEMT structure, 25 nm of Si3N4 are deposited in a low-pressure chemical-vapour-deposition (LPCVD) system from dichlorosilane (SiH2Cl2) and ammonia (NH3).39 On these samples, pulsed measurement-stress-measurement characterization studies as previously described in Ref. 24 are performed using a HP4200 with a gate bias from −25 V to 15 V.

III. RESULTS

Figure 1 schematically depicts the HEMT device structure (a) as well as the band diagram with respective interface states (b). During electrical stress and recovery measurements, those interface states are filled and emptied, respectively. In Fig. 2, the stress and recovery data of the standard (a) and fluorinated-interface device (b) are shown. Both devices were stressed at different biases from about −15 to +12 V for 100 µs without any prior stress. The monitoring of the drain current during recovery was performed at multiple gate biases24 in order to capture the whole drift dynamic with a threshold voltage shift of several volts. The comparison between the two devices [Fig. 2(c)] clearly shows that the standard device does not exhibit any measurable drift during negative gate bias and starts drifting only for positive biases. In clear contrast, the threshold voltage of the fluorinated device follows the stress bias in the positive and negative direction, suggesting fast emission as well as the capture of electrons at the interface. This mechanism is described in more detail elsewhere.24 The recovery characteristics suggest a much broader range of emission times for the standard device, which are typically assumed to be related to oxide traps.3,29 The much more confined defect states in the fluorinated device5 as well as the fast emission and capture times suggest that the interface defects follow a classical SRH defect model.4,24 We speculate that those additionally ionised donor-like interface defects could also be beneficial.

FIG. 1. The schematic HEMT structure and the discussed Si3N4/AlGaN interface are shown in (a). The respective band diagram is shown in (b).
with respect to surface passivation in the access region of a device. Typical negative charge trapping in the buffer, barrier, or at the interface could be compensated by those positive charges and therefore minimise the effect of any negative bias stress e.g., off-state condition or hot electron stress.40

From AES measurements [Fig. 3(a)], the physical-chemical effect of the surface fluorination is seen: remote plasma fluorination leads to a modification of the surface atomic composition compared to the reference AlGaN surface. Thus, the remote ICP-F creates an increase in surface electronegativity as the nitrogen atom is substituted by a fluorine atom.31 A surface coverage of up to 16% of F can be achieved by remote ICP-F. In contrast, the measured fluorine concentration after direct TCP-F is 20% [Fig. 3(a)]. This increase compared to remote ICP-F is explained by additional near-surface implanted F ions which are also detected by the AES measurement.

The increase in superficial F is attributed to near-surface Ga-F and Al-F bonds after the remote fluorination process [see XPS data in Fig. 3(b)]. N-F bonds cannot be found by XPS, which is in accordance with the literature32—however such N-F bonds may not be excluded.

Additionally, from the XPS, it is found that some C-F (25 at. %) bonds are present after the CF4 processing. In order to exclude that these bonds are related to a deposited polytetrafluoroethylene (PTFE)-like layer, the samples are also treated with the NF3 plasma, again leading to approximately 16% F at the surface. The NF3 remote-ICP fluorination yields 0.5 at. % C-CF species. In order to fully exclude the possibility of a hydrophobic fluorocarbon interlayer, the contact angles of the surfaces are measured and shown in Fig. 3(a). If a PTFE-like fluorocarbon layer was present, the contact angle would decrease (as it decreases with increasing hydrophobicity).29 The increasing diiodomethane contact angle (θd) after the surface fluorination on the other hand reflects the increasing hydrophilicity of the AlGaN surfaces, and hence, the surface dipole is enhanced by the F processing.29,33

Furthermore, the remote-ICP fluorination shows an exceptional stability in air: the value of the fluorinated AlGaN surfaces remains at 35 ± 2° for at least 180h. The F content decreases only slowly. As Fig. 3(a) shows, a F
amount as low as 1%–2% already increases the measured $\theta_d$. The same is true for the F content after heating the sample to 710 °C in a 700 mtorr NH3 atmosphere; the remaining F (0.8%) is therefore sufficient to maintain an increased $\theta_d$.

As the F concentration decreases over time, the oxygen concentration increases. Therefore, the desorbing F is most probably slowly substituted by an oxygen or hydroxyl unit derived from atmospheric O2 or H2O. Processing the samples after the remote ICP-F further with a remote ICP oxygen plasma for 5 min does not influence the atomic surface composition: with $\theta_d = 35°$ and F = 5.0 at. % and O = 12 at. %, it is very much comparable to the results after 24 h of storage (with $\theta_d = 35°$ and F = 4.6 at. % and O = 11 at. %). Therefore, O2 and its plasma-excited states are slowly competing with the surface fluorides. The wet cleaning of the remote ICP-F samples with 0.5% aqu. HCl or 0.5% aqu. HF removes all detectable F from the surface and decreases the $\theta_d$ to the original value of $15 ± 2°$. This clearly indicates that a removal of the fluorine by nucleophilic substitution of hydroxide (OH–) or water (H2O) is performed; hence, the Ga-F (or Al-F) can be exchanged to a Ga-OH (or Al-OH, Ga-H2O, or Al-H2O) termination, as suggested in the following:

$$\equiv Ga - F + OH^- \leftrightarrow \equiv Ga - OH + F^-,$$

$$\equiv Ga - F + H_2O^{+} \leftrightarrow \equiv Ga - OH + H^+ + F^-. \quad (2)$$

More detailed information on the adsorbates is obtained from the desorption analysis in Fig. 4: the mass effusion spectroscopy reveals that H2O (m/z = 18) and F (m/z = 19) mainly desorb at $T \leq 350°$C, along with other adsorbates like H2 or CO2. The comparison to the reference sample revealed a clearly lower m/z = 19 peak than the fluorinated sample. However, the presence of this m/z = 19 peak indicates that some fluorine is also present at the cleaned, not fluorinated, reference AlGaN surface. This is not necessarily surprising as the affinity of the polar III-N surface to atoms from the halogen group is high. Furthermore, the presence of F on the cleaned surfaces is not in contradiction to XPS or AES measurements, as the limit of detection lies at ~0.3% for these surface analysis techniques.

IV. DISCUSSION

The electrical behaviour (Fig. 2) of the MIS-HEMT after remote-ICP fluorination is very distinctive: from a comparison to other plasma surface processes (including direct TCP-F), it is gathered that only remote ICP surface fluorination results in the discussed modification of the dominant surface donor, independent of the plasma precursor gas. Surface treatments prior to dielectric deposition using other process gases (Cl, Br, O, as well as F-TCP plasma) result in device behaviour comparable to the untreated interface (Table I). It is interesting to note that even mixing oxygen into the remote-ICP F-plasma or subsequent oxygen plasma does not remove the surface fluorination effect. Additionally, simple electron irradiation can be excluded as we did not observe charging effects during processing. Even though the interplay of radicals and ions in plasma systems is very complex, the significant difference of surface fluorination in the remote plasma compared to the direct plasma could be that more radicals and fewer ionic species exist that will participate in surface reactions or even ion implantation.

In the case of NF3, there are three simplified dominant types of fluorine species available for reaction in the plasma: fluorides (F–, including NF–, NF2–, and NF3–), fluorine radicals (F•, including NF••, NF2•, and NF3•), and fluorine cations (F+, including NF+, NF2+, and NF3+) as well as complexes of their educts. Among those, only F–, F+, and F can be

<table>
<thead>
<tr>
<th>MIS HEMT surface treatment</th>
<th>$V_{th}$ [V]</th>
<th>Trap dynamic</th>
</tr>
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<tbody>
<tr>
<td>Remote ICP-F</td>
<td>−15</td>
<td>Fast</td>
</tr>
<tr>
<td>Remote ICP-O2</td>
<td>−6</td>
<td>Slow</td>
</tr>
<tr>
<td>Remote ICP-F + ICP-O2</td>
<td>−15</td>
<td>Fast</td>
</tr>
<tr>
<td>Remote ICP-F + 180 h storage</td>
<td>−15</td>
<td>Fast</td>
</tr>
<tr>
<td>Remote ICP-F + NH3 700 °C, 30 min</td>
<td>−15</td>
<td>Fast</td>
</tr>
<tr>
<td>Remote ICP-F + Aqu. HF or HCl clean</td>
<td>−6</td>
<td>Slow</td>
</tr>
<tr>
<td>Direct TCP-F</td>
<td>−2</td>
<td>Slow</td>
</tr>
<tr>
<td>Aqu. cleaned reference</td>
<td>−6</td>
<td>Slow</td>
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found independent of their F-precursor e.g., CF₄ and SF₆. As the concentration of C-CF species at the surface is low [Fig. 3(b)], we can assume that mostly fluorine and its ions interact with the surface.

On the one side, the negative polarization charge at the AlₓGa₁₋ₓN (0001) surface might be expected to attract positively charged ions. This has been reflected in improved wetting behaviour measured by contact angular analysis for solvents with increasing electron-accepting properties. However, any positive or neutral F atoms in the plasma will readily accept electrons and therefore become F⁻ before they reach bonding distances: F has a high electron affinity (3.4 eV), and the affinity level shifts down further when approaching a surface. Assuming a work function of \( \approx 4 \text{ eV} \) for GaN, tunneling from the conduction band will easily fill the F affinity level. This expectation is supported by the F bonding to the group-13 metal atoms in the surface region [Fig. 3(b)]. Furthermore, since c-plane AlGaN is supposed to terminate in metal rich reconstructions, it is more likely that the Lewis bases (electron donors, like F⁻) from the plasma will react with a surface metal atom.

Nonetheless, based on the distinctive electrical results after direct TCP-F and remote ICP-F (Table 1), we can compare the differences in the two plasma conditions:

- The main advantage of the remote ICP-F plasma is suggested to be the high concentration of F⁻ which can diffuse to the III-N surface. Here, it allows a soft impact fluorination in contrast to TCP-F where accelerated ions impinge on the surface. The character of the soft fluorination is based on the high reactivity and sufficient excitation energy to break a near-surface bond without charging the surface.

One possible explanation for the electrically observed surface modification is that F⁻ is responsible for a modification of the surface donor state. The interface trap level in the standard AlGaNa/GaN MIS HEMT has been shown to be at about 6 eV below the conduction band minimum (CBM). In contrast to this, the fluorine-modified surface donor lies at approximately 1.3 eV below the CBM. If we assume that hydroxide bonds are responsible for the native surface donor at around 0.8 eV, a modification of OH⁻ surface concentration will lead to the modified donor behaviour. As both F⁻ and OH⁻ are nucleophiles and compete over the same available Ga(Al) bonds, the proposed reaction mechanism (Eqs. 1 and 2) could be the part of the surface modification or is at least partly responsible for the electrical behaviour. Thus, the new extrinsic surface trap could result from an exchange of the superficial hydroxide with the fluoride. This is further supported by the removal of the fluorination with aqueous cleans [Fig. 3(a)], causing the AlGaN surface to return to the native surface donors.

However, as mentioned earlier, the effusion analysis shows that F is also present at the standard surface. Further analysis by secondary ion mass spectroscopy (SIMS, Fig. 5) of the fluorinated as well as the standard AlGaN surfaces, both passivated with Si₃N₄, reveals comparable amounts of F atoms at both interfaces. The extracted F concentration is around \( 6 \times 10^{12} \text{ cm}^{-2} \) in both cases. This means that most of the superficial fluorine desorbed before Si₃N₄ deposition at 700°C. For comparison, a direct TCP-fluorinated sample is shown, exhibiting the same amount of F at the interface as well as an additional F contribution caused by F implanted into the AlGaN layer. Hence, the resulting F concentration after dielectric deposition at the interface is completely independent of the applied surface modification method. Considering potential matrix effects during the SIMS measurements, it is still a remarkable high quantity of F on the non-fluorinated devices and it is not completely clear where F comes from this case. Nevertheless, even though F is present at the standard as well as the remote ICP-F AlGaN surfaces, the electrically observed behaviour is indeed dependent on and solely achievable by the remote ICP fluorination process. Thus, the detected F atoms might be bound differently in those cases and their role in the surface modification is not clear. However, we recognize that the contact angle \( \theta_d \) after remote ICP-F plasma and subsequent high temperature NH₃ treatment remains different from the surface with the same thermal treatment without plasma exposure [Fig. 3(a)]. Therefore, not only an electrical difference after Si₃N₄ passivation but also a modification of the surface itself are clearly indicated after fluorine-species (e.g., HF, GaF₃, or similar) desorption from the processed GaN surface.

Summarizing all the above, it allows two quite contrary hypotheses: F is directly responsible and represents the new donor state. Thus, there must be a bonding difference between the F after remote-ICP fluorination and the F that is otherwise present at the surface. In addition, an interference of the F with the deposition of Si₃N₄ cannot be excluded from our results. However, its bonding information is unclear because our experiments show an insufficient amount of F (\( \leq 1\% \)), remaining at the interface to be detected and conclusively interpreted by XPS. The limitation of physical analysis techniques is a major obstacle in the analysis of the origin of the GaN surface donor because the 2DEG electrons derive from around \( 1 \times 10^{13} \text{ cm}^{-2} \) surface defect states and hence <1% of the actual surface concentration (XPS always
detects at least a few monolayers, thus reducing the amount of detectable F even further. From SIMS data, only approximately $6 \times 10^{-12} \text{cm}^{-2}$ F atoms are obtained. Therefore, an extraction of the exact chemical origin of the surface donor still remains reserved at this point.

In another possible interpretation, F is only indirectly responsible for the modified surface potential. In that case, the remote ICP-F plasma treatment could cause an exchange of the hydroxide with the fluorine surface groups [as described in Eqs. (1) and (2)]. The surface modification is stable in air but fluorine will be desorbed during the thermal treatment prior to the dielectric deposition (as shown in Fig. 4). Fluoride can carry less charge than an oxide or nitride, and thus, one N$^{2-}$ has to be substituted by three F, which will lead to structural changes at the surface. Even though fluorine is desorbed subsequently, its modification of the surface might remain, either by simply creating a new stable surface reconstruction or by making dangling bonds available for the reaction with the atoms/precursors during dielectric deposition.

V. CONCLUSIONS

In this work, it has been shown that the remote plasma fluorination of AlGaN surfaces leads to a modification of the interface donor state. The electrical drift measurements of HEMTs are compared to physical surface and interface analyses. Even though the exact physical origin of the surface donor cannot be extracted, it is clear that the AlGaN surface after the remote plasma fluorination is more defined. From surface and interface analyses, we suggest that the fluorine itself might not directly be the new surface donor but that it rather activates the AlGaN surface prior to the dielectric deposition.

ACKNOWLEDGMENTS

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