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Sidharth Suman, Brigitte Martin, Ludovic Dupre, Fabien Rol, Roselyne Templier, et al.. p-GaN Contact Study by Means of Electrochemical Short Loop. ECS Advances, 2022, 4 (1), pp.042502. 10.1149/2754-2734/aca07d . cea-04565939

**HAL Id: cea-04565939**

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Submitted on 2 May 2024

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# p-GaN Contact Study by Means of Electrochemical Short Loop

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Surface states and contamination affects the efficiency of Gallium Nitride (GaN) based devices such as HEMTs, LEDs, photodetectors etc. In this work, several wet chemical treatment has been performed for the surface treatment of p-GaN, in order to achieve low-resistance ohmic contacts. The effect of surface treatment is observed by studying the flatband potential across the p-GaN/electrolyte interface via, electrochemical characterization. The electrochemical method of “Mott-Schottky characterization” gives simple and quick way of analysing the effect of different treatments, without the need of device fabrication. The effect of surface treatment are further investigated via, X-ray Photoelectron Spectroscopy and Atomic Force Microscopy. The potential surface treatments from experimental findings are integrated into device processing steps in order to realize effect of surface treatment on the p-GaN/metal contacts. The electrochemical characterization shows that HCl results in least flatband potential. Further, The electrical test shows that HCl treatment results in significant orders of magnitude improvement in contact resistance and electrical performance of the devices. This shows that short loop electrochemical characterization can be used for predicting surface treatment in order to improve electrical characteristics of the device.

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Manuscript received November 1, 2022. Published November 17, 2022.

Supplementary material for this article is available [online](#)

Gallium Nitride (GaN) is wide bandgap semiconductor that have attracted wide attention in optoelectronic devices and electronic devices such as light emitting diodes (LEDs), Laser diodes (LDs), Photodetectors and High electron mobility transistors (HEMTs). The efficiency of GaN specially p-type GaN is limited in these devices, due to difficulty in forming reliable ohmic contacts. The high specific contact resistance of p-type GaN is due to several reasons:<sup>1</sup>

- Unavailability of metal with high work function. The work function of p-GaN is 7.5 eV, whereas the work-function of metals are typically less than 5.5 eV.
- Difficulty in achieving high doping concentration in case of p-GaN, due to the high ionisation energy of acceptor Mg  $\sim 170$  meV.
- Oxygen and Carbon contaminants and surface states.

Surface states and contaminants (mainly C and O) are important consideration for GaN based devices, as they affect the electrical and optical properties of devices. The surface states with energies within the electronic bandgap of GaN act as a trap states and affect the charge transfer across the interface. If the density of surface states are high enough, they cause fermi level pinning and the contact doesn't depend further on the work function of the metal.

The surface states result from dangling bonds, surface vacancies, and structural defects on the surface. Several wet chemical and dry etching process have been reported for the preparation of p-GaN surface before device fabrication.<sup>2</sup> Surface treatment is vital in device processing steps, it is required to remove surface oxides, carbon contaminants, adsorbates, minimise or passivate surface states to provide atomically clean surface.<sup>3</sup> To decrease the specific contact resistance, a high electrical conductivity or low barrier height at the interface is needed. Hence, for these devices high quality and reliable metal-semiconductor interface are very important consideration. Several wet chemical and dry etching process has been reported for the preparation of p-GaN surface before device fabrication. Lee<sup>4</sup> and J.Sun<sup>5</sup> report that boiling KOH treatment results in ohmic P-GaN contact formation, accounting to the less C and O contamination and less Ga/N ratio as compared to HCl treated sample. The work by Kim<sup>6</sup> and Lee,<sup>7</sup> report that the p-GaN treated

with aqua-regia and  $(NH_4)_2 S$  in sequence gives better contact resistivity. The aqua-regia removes the O and C contamination, and prevents re-oxidation during atmospheric exposure leading to the direct contact between metal and p-GaN surface. The contact resistivity for Pt contact on p-GaN reduces from  $(5.1 \pm 0.6) \times 10^{-1} \Omega \text{ cm}^2$  for HCl-treated to  $(2.5 \pm 0.3) \times 10^{-5} \Omega \text{ cm}^2$  by treatment with aqua-regia and  $(NH_4)_2 S$  in sequence. The authors of<sup>8</sup> also report decrease of surface band-bending after  $(NH_4)_2 S$  treatment, they accredited the decrease of band-bending to decrease of surface state related to nitrogen vacancy. The nitrogen vacancy are possibly occupied by sulphur in  $(NH_4)_2 S$ , leading to decrease in Ga/N ratio.

The work by Huh<sup>9</sup> reports three orders of magnitude decrease in contact resistance of p-GaN/Pt metal after the surface treatment of p-GaN with alcohol-based  $(NH_4)_2 S$ . The specific contact resistance decreased from  $2.56 \times 10^{-2} \Omega \text{ cm}^2$  for untreated to  $4.71 \times 10^{-5} \Omega \text{ cm}^2$  after alcohol-based  $(NH_4)_2 S$  treatment of p-GaN. The improvement in ohmic characteristic was due to effective removal of oxides and shift of surface fermi level towards the valence band edge. Some authors reported improvement in contact resistivity after treatment of p-GaN in boiling aqua-regia solution prior to metal deposition compared to HCl treatment.<sup>10,11</sup> The treatment with boiling aqua-regia results in removal of GaOx and removal of oxides leads to creation of Ga vacancy at the surface, which acts as acceptors. The Ga vacancy results in decrease of Ga/N ratio and shift of fermi level towards the valence band, hence, decrease in band-bending.

The goal of this study is to find potential wet-chemical surface treatment to be integrated in the device processing steps, in order to achieve low-resistance ohmic contact. Apart from finding suitable treatment, different characterisation techniques has been used to define methodology for characterising and comparing surface treatment. First the electrochemical capacitance-voltage characterization method has been used to study the transfer of charges and access barrier height after different treatment. After surface characterization study such as, X-ray Photoelectron Spectroscopy and atomic force microscopy was used to investigate the changes in elemental composition at p-GaN surface, changes in Ga and N stoichiometry and surface roughness etc Finally, the wet-chemical surface treatment are integrated into TLM fabrication processing and the effect of wet-chemical treatment are characterised by electric prober I-V characterisation.

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## 2. Experimental Method

A 8-inch (001)GaN sample grown by MOCVD on Si Substrate supplied by ENKRIS manufacturer was used for this study. Magnesium (Mg) was used as dopant for p-type doping of GaN. The Mg doping concentration of p-GaN is  $\sim 1 \times 10^{19} \text{ cm}^{-3}$ . Prior to wet-chemical treatment, all p-GaN samples were prepared by degreasing in acetone, isopropanol followed by rinsing in water and blow dry in  $\text{N}_2$ . One p-GaN sample was left untreated and other three p-GaN samples were treated with concentrated HCl, Piranha Acid (3:1  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ ) and  $(\text{NH}_4)_2\text{S}$  solution respectively. The samples were treated just before performing the experiment, in order to minimise atmospheric exposure.

**Electrochemical characterisation.**—A home-made three-electrode setup was used for performing the electrochemical experiment. The electrochemical set up consisting of Ag/AgCl as reference electrode, platinum as counter electrode and p-GaN sample as working electrode. The p-GaN sample was mounted inside lab-fabricated holder that exposed a circular area of  $0.28 \text{ cm}^2$  and electrical connections are protected from electrolyte thanks to the teflon part. The electrolyte was prepared by mixing 100 mM of NaCl and 50 mM of TRIS (Tris(hydroxyethyl)amino-0methane) into distilled water. Prior to experiment, the electrolyte solution was purged with  $\text{N}_2$  for period of 30 min in order to make the solution oxygen-free. After  $\text{N}_2$  purge, the p-GaN samples were introduced into electrolyte to perform the experiment. All the experiments were performed in dark inside faraday cage at room temperature.

Different surface-treated p-GaN samples were studied by Cyclic Voltammetry, Impedance Spectroscopy and Mott-Schottky method. While cyclic voltammetry and Impedance Spectroscopy is widely used experimental technique; Mott-Schottky, is a special type of electrochemical impedance spectroscopy that is used in case semiconductor material study. Mott-Schottky method is plot of inverse of square of capacitance  $1/C^2$  with respect to applied potential V vs Ag/AgCl reference electrode. The slope of this plot gives doping density (acceptor density  $N_a$  in case of p-type) and intercept gives the flatband potential  $V_{fb}$ . The cyclic voltammetry was performed at scan rate of  $20 \text{ mV s}^{-1}$ . The impedance spectroscopy was carried out for wide frequency ranging from 1 Hz to 100 kHz at DC bias of 0 V, with AC modulation amplitude set to 20 mV. The Mott-Schottky experiment was carried out from  $-0.4 \text{ V}$  to  $1 \text{ V}$ , for frequency ranging from 1 Hz to 100 kHz and AC modulation amplitude of 20 mV. The Mott-Schottky technique is used to find the band-bending of p-GaN after different treatment. The charge transfer across the semiconductor/electrolyte depends on the oxides, surface states, contaminants and surface reconstruction. Furthermore, these defects and contaminants can be altered by applying different surface treatments, resulting in difference in charge transfer across the semiconductor/electrolyte interface.<sup>12,13</sup> The treated p-GaN samples have different levels of oxides, surface states and impurities. It will result in different amount of charge flow across p-GaN/electrolyte interface and hence, different band-bending for p-GaN. Mott-Schottky characterisation technique is used to find the band-bending and energy level of p-GaN. The Mott-Schottky characterization technique of electrochemical impedance spectroscopy has not been reported widely for p-GaN. This is due to the critical behavior of p-GaN such as difficulty in making contact, high resistivity, sensitivity to get oxidised in atmosphere, high density of surface and interface states etc. The results obtained for p-GaN have been analysed based on the understandings from n-GaN experiments. The Mott-Schottky protocol was first validated on n and p-type Si. The details of n-Si, p-Si and n-GaN are discussed in results and supplementary article.

**Surface characterisation.**—Surface characterisation were performed using X-ray photoelectron spectroscopy and atomic force microscopy. X-ray Photoelectron spectroscopy (XPS) analysis was performed to determine the surface composition of different

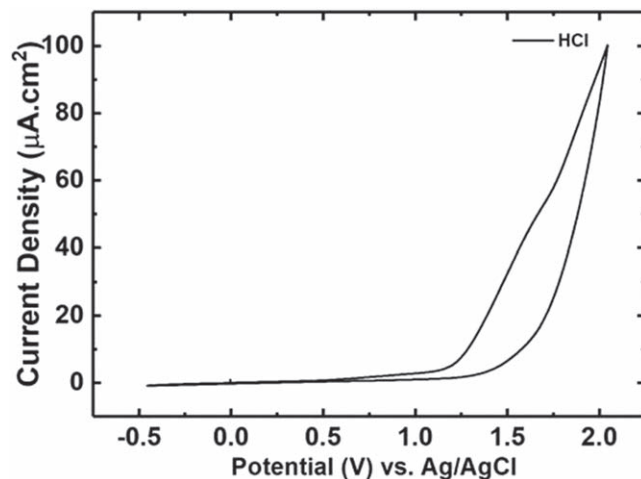
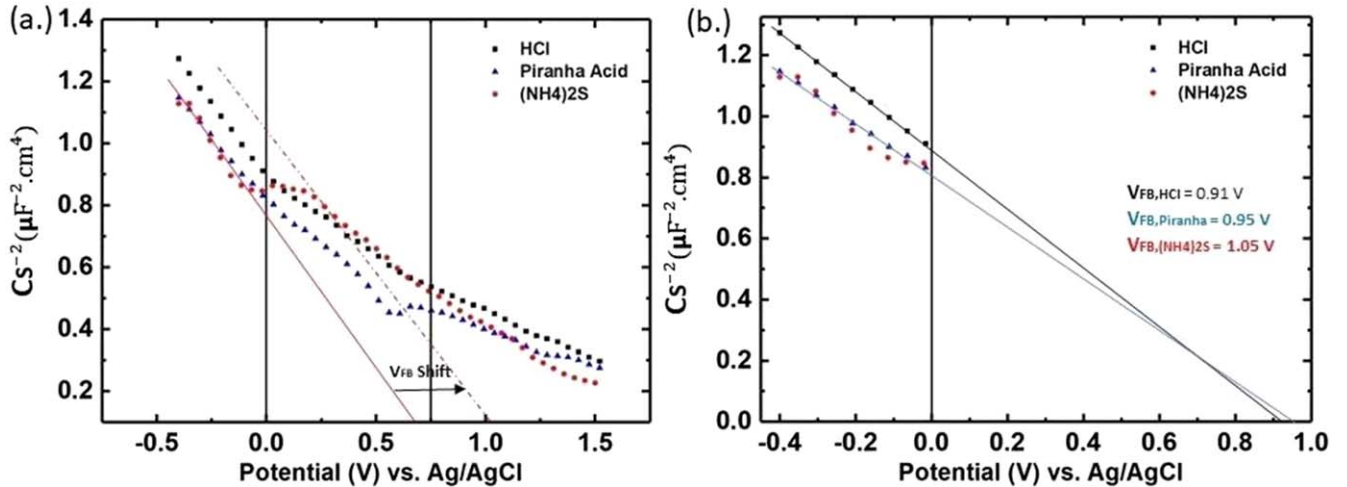


Figure 1. Cyclic-voltammetry of HCl treated p-GaN.

elements, change in stoichiometry and shift in fermi level at p-GaN surface. XPS analysis was performed with PHI500 VERSAPROBE II X-ray spectrometer instrument, with the monochromatized X-ray radiation emitted by an anti-cathode of Al ( $E_{k\alpha} = 1486.6 \text{ eV}$ ). The XPS signals were recorded at grazing angle of  $45^\circ$ . The maximum probed depth was 8 nm, with 63% of signals coming from first 2.8 nm depth on the surface. Lateral resolution was 0.5 eV. X-Ray chamber was maintained at ultra-high vacuum for performing the experiment. The p-GaN samples were treated in different chemicals and transferred to the XPS sample holder in  $\text{N}_2$  atmosphere, without air-break. This was done to prevent re-oxidation of p-GaN during atmospheric exposure. CASA XPS software was used to analyse the results obtained from the XPS experiment.

Atomic Force Microscopy (AFM) was performed to determine the surface roughness after different wet-chemical treatments. Bruker Dimension Icon instrument was used to record surface topography scan in tapping mode for p-GaN samples. The samples were treated with different chemicals just before the AFM measurements, to minimise atmospheric exposition.

**Transfer length method.**—After electrochemical and surface characterizations, Transfer Length Method (TLM) was fabricated, in order to investigate the effect of surface treatment on the electrical characteristics. TLM is widely known method for determining the contact resistance and specific contact resistivity.<sup>14-17</sup> An array of linear and circular TLMs were fabricated, with varying spaces between them. The TLM arrays were fabricated using photolithography and etching of mesas towards n-GaN layer by inductive coupled plasma etch (ICP etch) method. The surface treatments were integrated in the fabrication process. The HCl,  $(\text{NH}_4)_2\text{S}$  surface treatment were integrated in TLM formation via Lift-off method, whereas Piranha acid was integrated in TLM formation via Etching method. The Ni/Au 10 nm/50 nm metal contacts were deposited using electron beam depositor. TLM arrays were annealed at  $500^\circ\text{C}$  for 5 min in presence of 4:1  $\text{N}_2/\text{O}_2$  atmosphere. The annealing was performed to improve metal adhesion and further improve the contact. SEM characterization was used to see the surface morphology after lift-off, to observe the deposited contact and microstructure evolution that could lead possible flaws and results in high contact resistance. The electrical characterisation was performed using probe methods at the room temperature, to see whether the contact leads to ohmic or schottky contact. The linear I-V characteristic represents ohmic behavior with less specific contact resistivity whereas the non-linear I-V characteristics represents Schottky behavior with high specific contact resistivity. In the TLM Method, the total resistance of TLM metal contacts with varying distance are measured and plotted as function of distance.



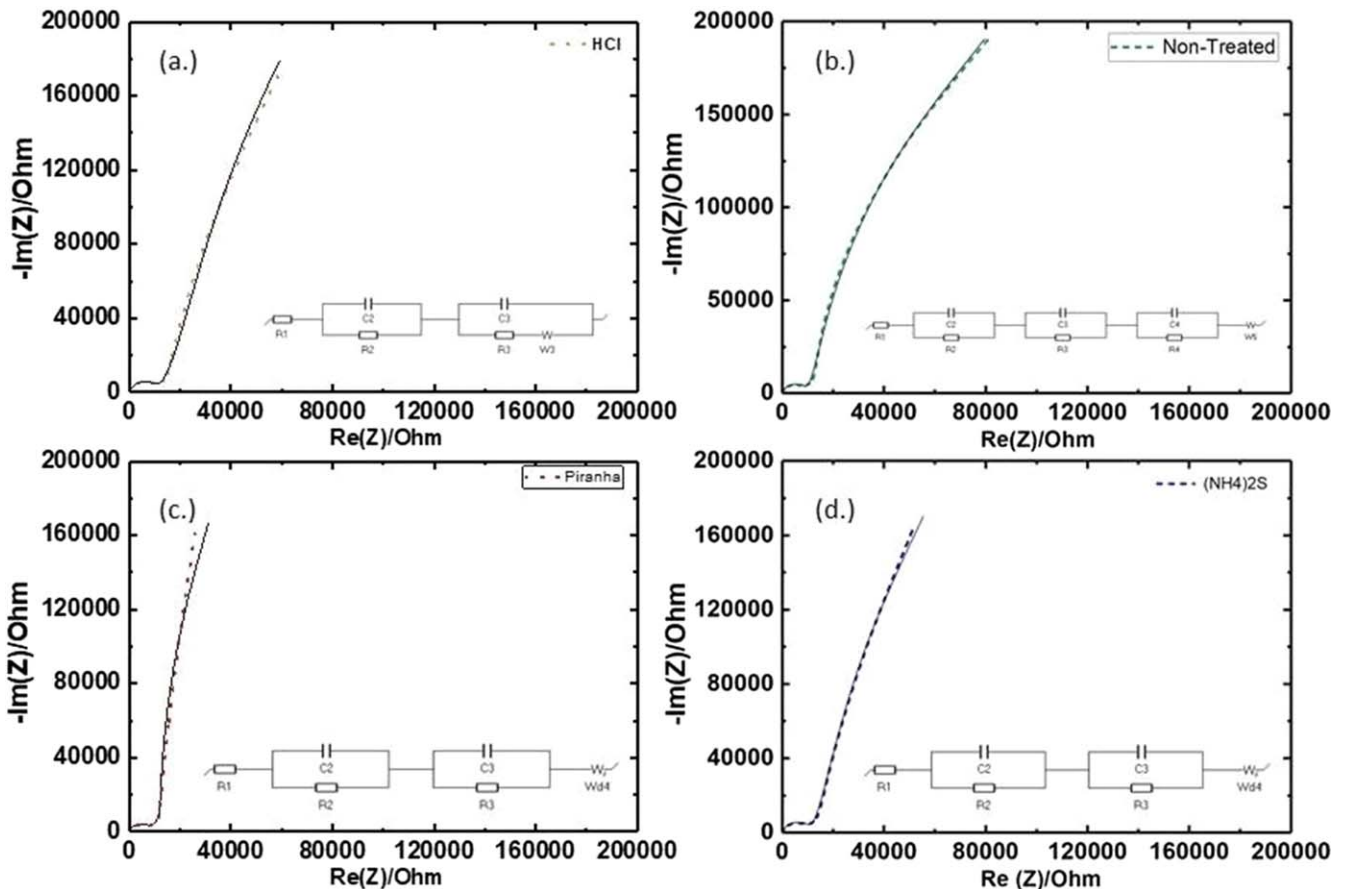
**Figure 2.** Mott-Schottky plot of HCl, Piranha acid and  $(NH_4)_2S$  treated p-GaN respectively (a) showing different regions (b) in reverse bias depletion regime which is region of interest to obtain doping density and flatband potential.

By extrapolating the total resistance to distance equal to zero gives the contact resistance and slope of the graph gives the sheet resistance. From the contact resistance, sheet resistance and transfer length, the specific contact resistivity is obtained. Different surface treatment of p-GaN will result in different I–V characteristics as well as different specific contact resistivity.

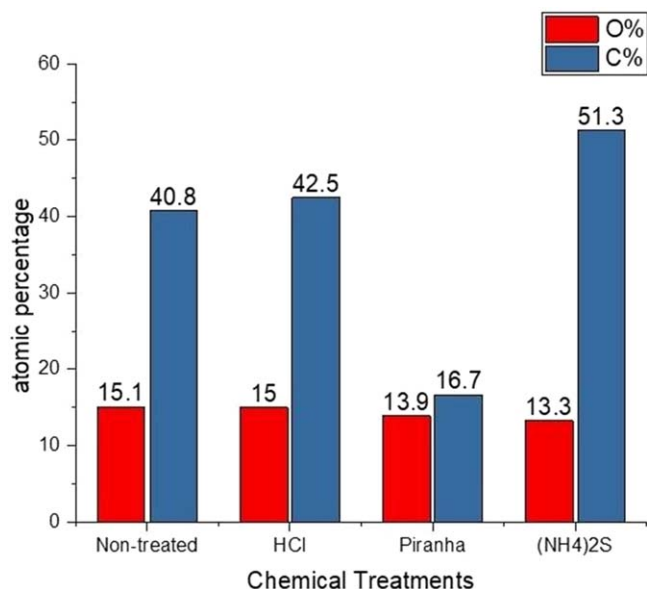
**Results and Discussion**

**Electrochemical interface study.**—The Mott-Schottky protocol was first validated on n and p-type Si. The resulting Mott-Schottky

curve was linear for both p-Si and n-Si. The doping density of n-Si and p-Si were  $4.15 \times 10^{20} \text{ cm}^{-3}$  and  $3.14 \times 10^{20} \text{ cm}^{-3}$  respectively, and the flatband potential obtained was  $-0.68 \text{ V}$  and  $0.45 \text{ V}$  vs Ag/AgCl for n-Si and p-Si respectively. The doping density obtained was in same range as expected theoretical value from the manufacturer. The obtained flatband potential of n-Si and p-Si was in same range as reported earlier and the sum of their flatband potential is close to 1.1 eV (bandgap of Si).<sup>18,19</sup> This confirms that our electrochemical set up produces reliable results. The n-Si and p-Si are shown in supplementary material (Figs. S1 and S2). After the Si samples, the mott-schottky characterization was performed on dil.



**Figure 3.** Equivalent electric circuit model for impedance spectra of (a) HCl (b) Non- treated (c) Piranha acid and (d)  $(NH_4)_2S$  treated p-GaN respectively.



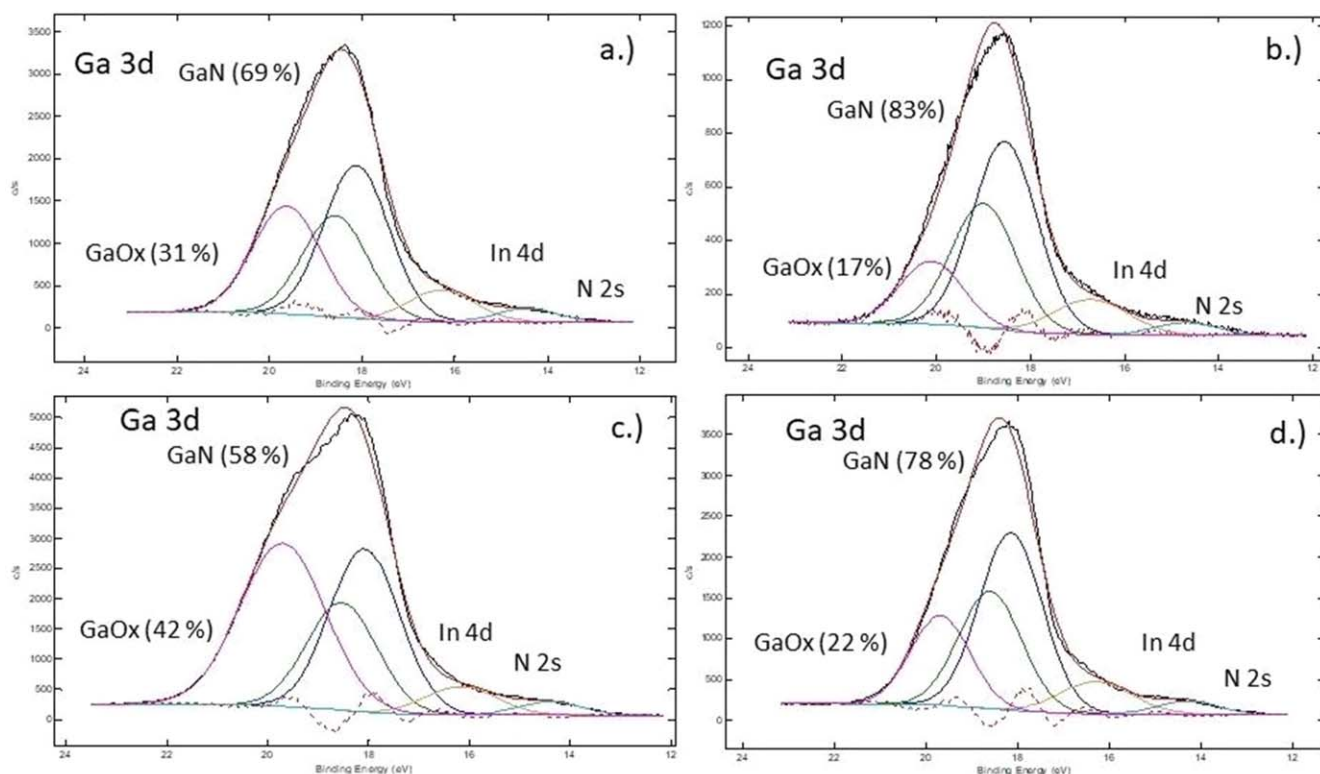
**Figure 4.** O and C percentage for non-treated, HCl, Piranha and  $(NH_4)_2S$  treated p-GaN.

and conc. HCl treated n-GaN. Mott-Schottky plot for n-GaN showed ideal linear plot until  $-0.5$  V after their was bent in linear curve possibly due to the charge transfer via surface states.<sup>12,13,20</sup> The cyclic voltammetry and mott-schottky curve for n-GaN is shown in supplementary material (supplementary Figs. S2(a) and S2(b)).

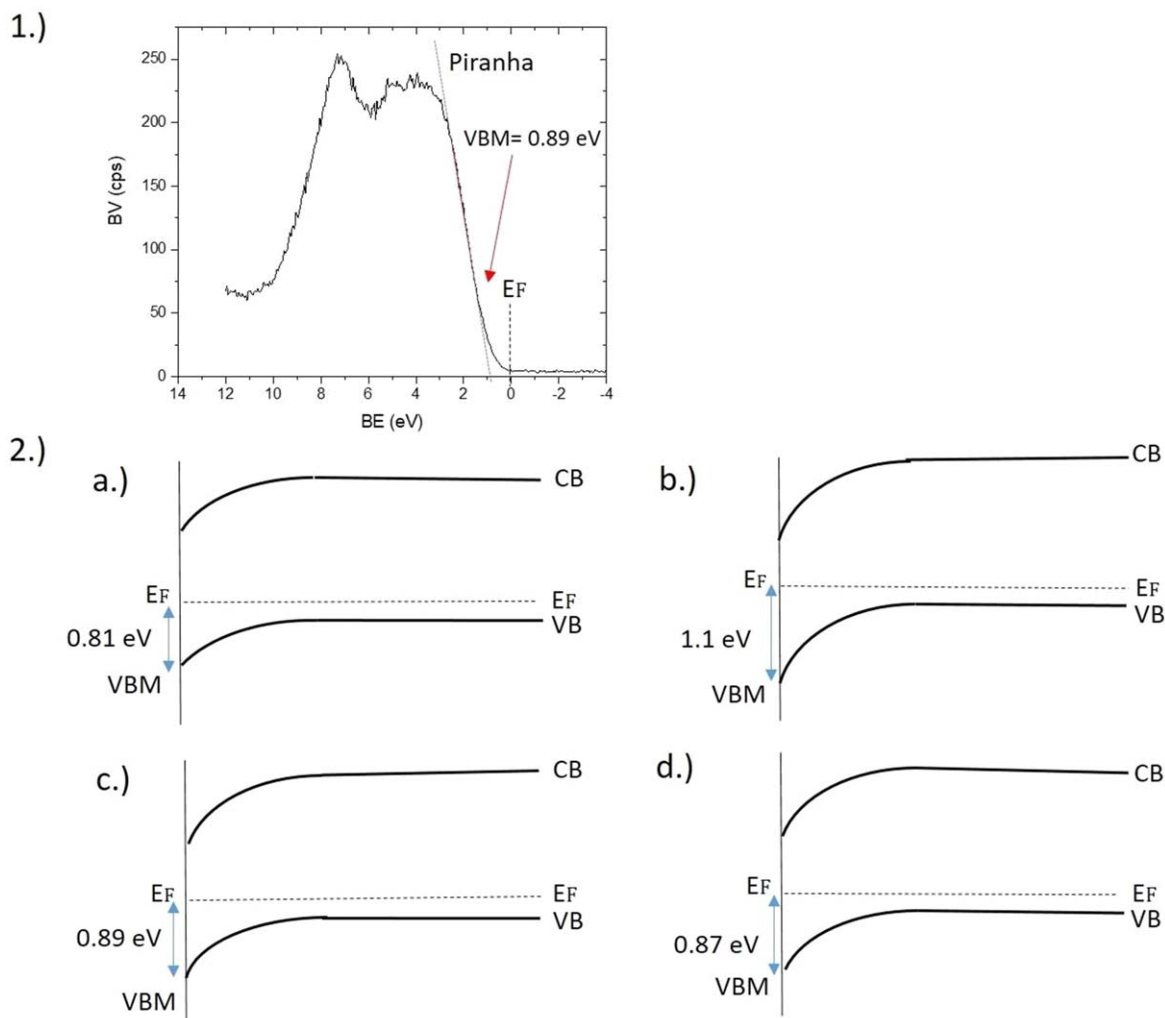
Later, the cyclic voltammetry, impedance and mott-schottky was performed on p-GaN sample treated with different chemistry, in a wide range of voltage and frequencies inside Faraday Cage in dark. The HCl treated p-GaN sample was taken as reference sample, as HCl is most widely used chemistry for p-GaN treatment in device

processing. The cyclic voltammetry was performed to find the depletion regime for mott-schottky plot. Figure 1 shows the cyclic voltammetry of HCl treated p-GaN. The cyclic voltammetry was performed in the voltage range from  $-0.5$  V to 2 V vs Ag/AgCl. The potential window was taken carefully by taking the no current region between  $-0.5$  V to 0.5 V corresponding to depletion region. The anodic current peak starts to appear at potential more positive than 0.8 V vs Ag/AgCl, this peak is due to the oxygen evolution in aqueous electrolyte. After finding the potential window, the Mott-Schottky experiment was performed in the frequency ranging from 1 Hz to and 100 kHz. Figure 2 shows the Mott-Schottky plot for p-GaN sample treated with HCl, Piranha and  $(NH_4)_2S$  in dark respectively. The circular dots are the data obtained from the experiment, and the linear line is fitting. The Mott-Schottky plot for non-treated sample was not measurable, due to high level of oxides and surface states/contaminants the plot was not ideal. As observed from the Mott-Schottky plot for different chemicals, different treatments gives same behavior but there is shift in data points of p-GaN treated with different chemistries. Mott-Schottky plot shows 3 different regions, depending on change in slope:

- Reverse voltage depletion regime, Region 1: the region 1 with potential between  $-0.4$  V and close to 0V vs Ag/AgCl corresponds to the reverse voltage depletion regime for p-GaN. This is region of interest for Mott-Schottky to take the slope and intercept; the slope gives the doping density and the intercept gives the flatband potential. In this region the capacitance changes sharply with respect to applied voltage. It was observed that region 1 slope changes with change in acceptor density, this is observed by performing Mott-Schottky characterisation of p-GaN with two different dopant density. The slope was varying with doping density only in region of interest as shown in supplementary Fig. S3, further confirming that this region of interest for finding doping density and flatband potential.
- Region 2: the region 2 with potential between 0 V to close to 0.7 V vs Ag/AgCl corresponds to the region where the change in capacitance with respect to applied potential is very small. This



**Figure 5.** De-convoluted Ga3d peaks for (a) Non-treated, (b) HCl, (c) Piranha and (d)  $(NH_4)_2S$  treated p-GaN.



**Figure 6.** (1) Valence Band Spectra of p-GaN after Piranha treatment, (2) An approximate band-bending obtained for (a) Non-treated, (b) HCl, (c) Piranha and (d)  $(\text{NH}_4)_2\text{S}$  treated p-GaN.

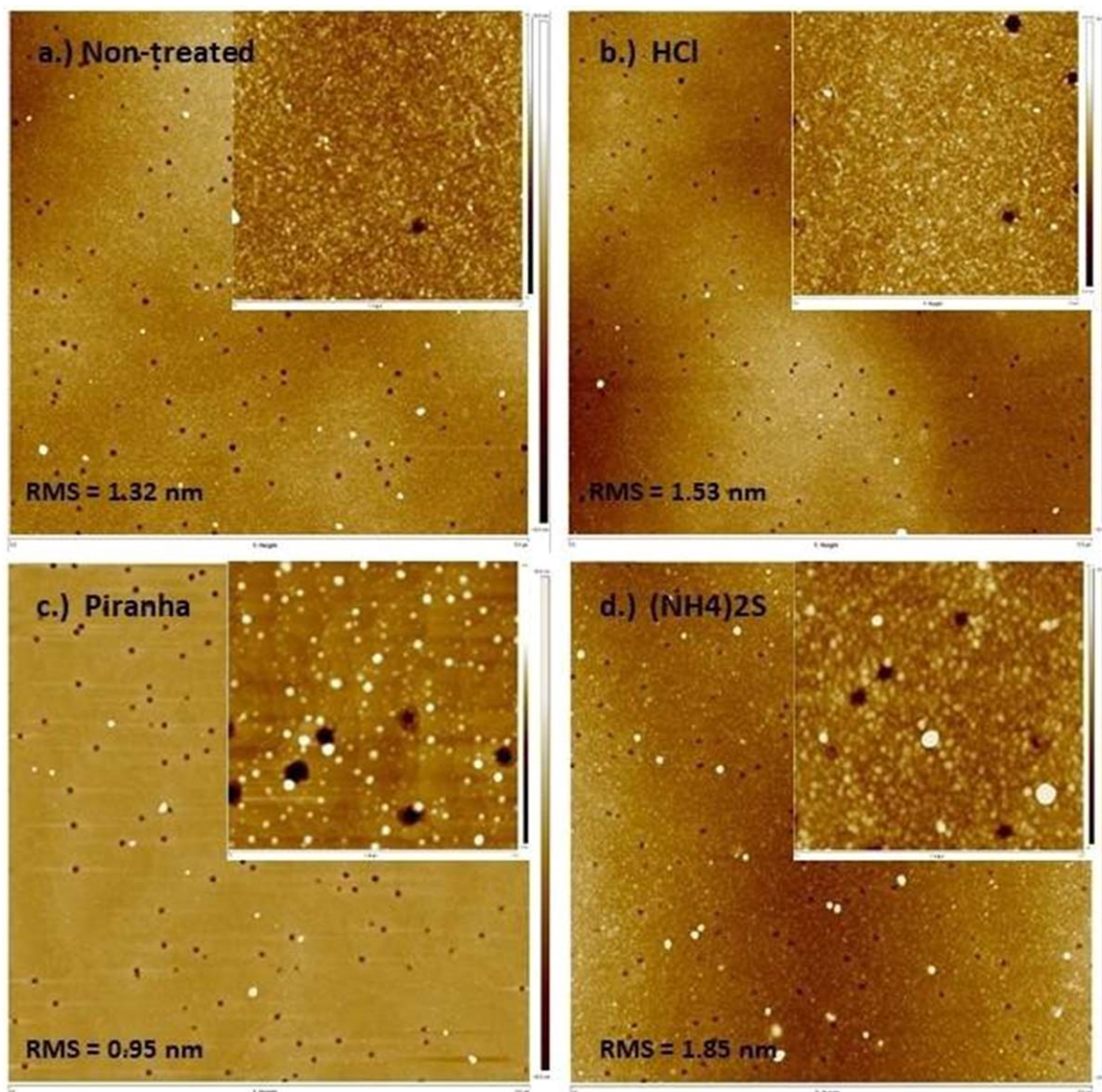
region probably represents the region, where the charge transfer to fill up the surface states.

• Accumulation region, Region 3: the region 3 with potential between 0.7 V and 1 V vs Ag/AgCl corresponds to the accumulation region. In this region capacitance changes minimally with respect to applied voltage, as there is no flow of charge across the GaN/electrolyte interface. This region results close to constant slope for inverse of capacitance square with respect to applied potential. The reverse-biased depletion regime/region 1 was used to find the doping density and flatband potential of p-GaN. Mott-Schottky linear extrapolation gave the acceptor density of approximately  $1.4\text{--}1.5 \times 10^{19}\text{ cm}^{-3}$  and flatband potential in range of 0.91 V to 1.25 V. The obtained doping density was similar to expected doping density from manufacturer. Knowing the open-circuit potential, doping density and flatband potential; the barrier height for p-GaN/electrolyte interface was calculated. The method to calculate barrier height from flatband potential, acceptor density and open-circuit potential is shown in Supplementary material (Supplementary Fig. 4). Table I shows flatband potential, doping density and barrier height after different wet-chemical treatments. HCl treated p-GaN has least barrier height compared to  $(\text{NH}_4)_2\text{S}$  and Piranha treated p-GaN, probably due to efficient removal of oxides.  $(\text{NH}_4)_2\text{S}$  treated p-GaN showed non-linear curve in shape of plateau and resulting in shift of flatband potential. The plateau shape is critical signature of Sulphur surface states on the surface. In the later part, XPS characterization

has been discussed to focus more on the elemental changes on p-GaN surface.

The equivalent electric circuit for the different treated p-GaN was obtained by fitting the impedance data in the EC-Lab Z-fit. Figure 3 shows the equivalent electric circuit model for different treated p-GaN. R1 represents the series electrical resistance accounting for ohmic drop in the circuit, R2 and C2 represents electrical double layer capacitance and resistance, R3 and C3 represents depletion region resistance and capacitance and W represents the Warburg element accounting for diffusion. W diffusion element depends on the surface of p-GaN/electrolyte interface. The W element is in parallel with double layer capacitance for HCl treated p-GaN, while in series for all other p-GaN samples. This is due to variation in diffusion phenomena at the surface.<sup>21,22</sup> The non-treated p-GaN had extra resistance R4 and capacitance C4, due to surface states resistance and capacitance on p-GaN/electrolyte interface. This further confirms that non-treated p-GaN has more oxide or contamination, and due to this it was not possible to obtain ideal mott-schottky curve.

**Surface study.**—X-ray Photoelectron Spectroscopy is most widely used surface characterisation technique for semiconductors. Angular dependent XPS was performed to find surface atomic concentration of different elements and band-bending in p-GaN after different chemical treatments.

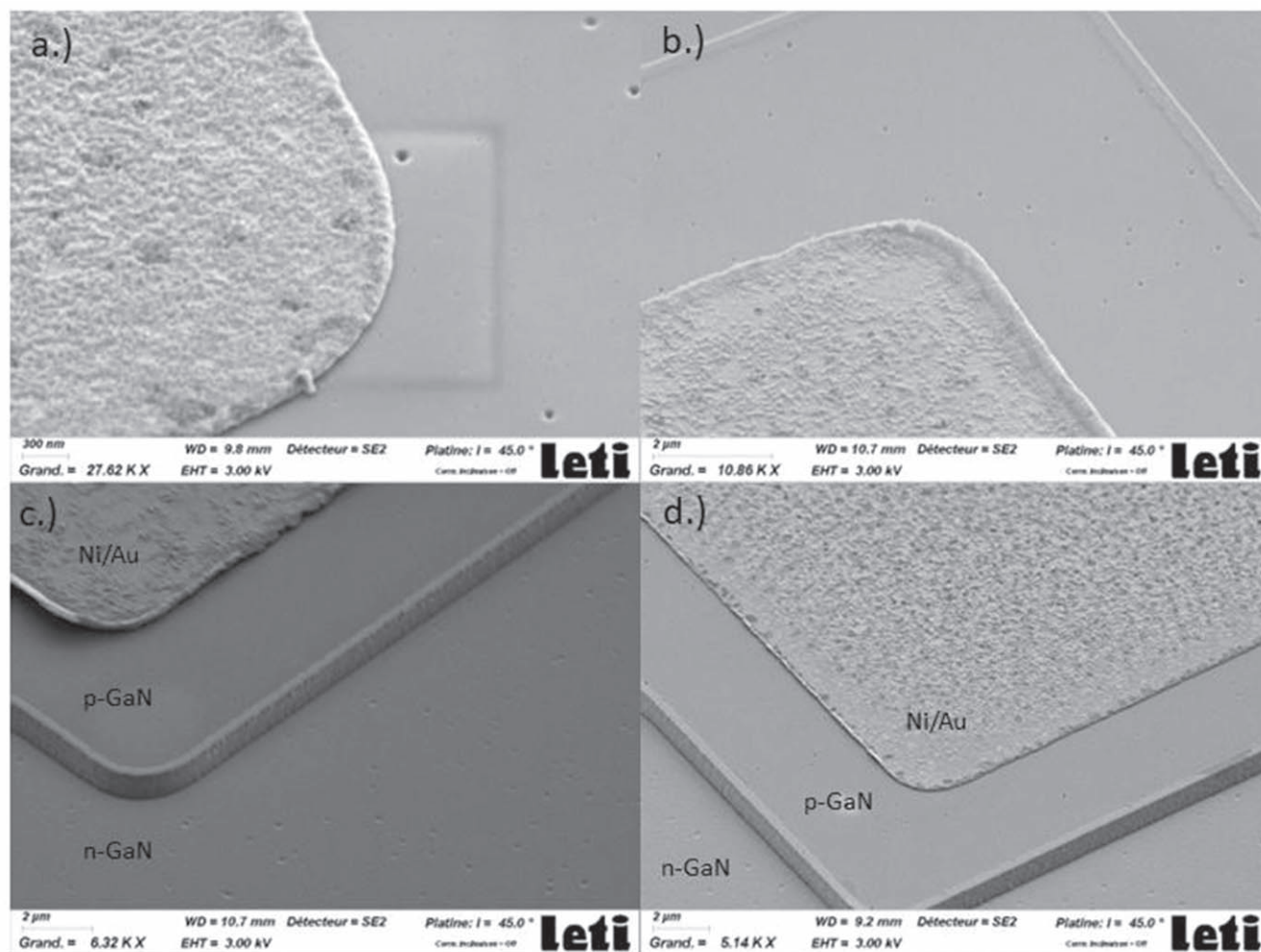


**Figure 7.** A  $5\ \mu\text{m} \times 5\ \mu\text{m}$  AFM image with inset  $1\ \mu\text{m} \times 1\ \mu\text{m}$  image of p-GaN with (a) Non-treated, (b) HCl, (c) Piranha acid and (d)  $(\text{NH}_4)_2\text{S}$  chemical treatment respectively.

XPS spectrum of the HCl treated p-GaN sample in wide range of binding energies (0–1200 eV) was obtained as shown in Fig. S5, Supplementary article. The wide-range spectrum shows carbon and oxygen peaks, showing that these are two major impurities present on the surface of p-GaN. The atomic ratios of all different elements (Cx, x = Ga, N, O, C, Cl and S) was obtained by integral peak intensities Ix of Ga 3d, N 1s, C1s, O1s, Cl2p and S2p respectively. (Supplementary Fig. S6 shows HCl-treated p-GaN core level spectra of Ga3d, C1s, O1s and N1s respectively) The elemental concentration and surface composition of p-GaN changes depending on the chemical treatment. The surface treatment results in removal of the carbon and oxides on the surface, and also modify the surface of p-GaN. Figure 4 shows the atomic ratios of C and O contamination on the surface after different chemical treatments. The piranha treated p-GaN results in least O and C contamination, whereas non-treated and HCl has high level of C and O contamination. The  $(\text{NH}_4)_2\text{S}$  treatment gives least Oxide content on surface. Apart from removing C and O, the chemicals such as HCl and Piranha acid also results in formation of new impurities of Cl and S on the surface respectively. These impurities can have adverse effect on the device formation: the Cl and S can be good for GaN-metal contacts to increase the adhesion the metal contact, however for a field effect devices the Cl

and S may results in additional defects for GaN-oxide contact.<sup>23,24</sup> The Ga3d peak was further de-convoluted into GaN and GaOx component, to study the surface composition. Figure 5 shows the de-convoluted Ga 3d peaks for non-treated, HCl, Piranha, and  $(\text{NH}_4)_2\text{S}$  treatment respectively. The de-convolution of Ga3d shows two peaks, one close to 19 eV and other close to 20 eV belonging to GaN and GaOx component respectively. The peak de-convolution shows that Piranha has 42% of Ga3d/GaN in GaOx form, this can be due to oxidation of Ga into  $\text{Ga}_2\text{O}_3$  form or due to formation of Ga-OH.<sup>25</sup> The GaOx was not further de-convoluted into  $\text{Ga}_2\text{O}_3$  and Ga-OH, however both the peak have binding energy close to each other.<sup>25</sup> The more Ga-OH form for Piranha treatment indicates hydroxylation of p-GaN surface, hence resulting in passivation of contaminants and surface states. Compared to Piranha, all other chemistries had much lesser Ga3d in GaOx form. Piranha acid treatment resulted in less oxygen contamination, but more gallium in gallium oxide form resulting in more band-bending compared to non-treated and  $(\text{NH}_4)_2\text{S}$  treatment.

Furthermore, the position of valence band maxima (VBM) was extracted with respect to the fermi level position, this distance gives approximately the band-alignment of p-GaN at the surface after respective chemical treatment.



**Figure 8.** SEM image after TLM structure formation for (a) Non-treated, (b) HCl, (c) Piranha and (d)  $(NH_4)_2S$  treated p-GaN.

**Table I.** Summary of doping density, flatband potential and Barrier Height obtained after different chemical treatments.

Treatments	Non-Treated	HCl	Piranha	$(NH_4)_2S$
Doping Density at $E + 19. \text{cm}^{-3}$	non-measurable	1.4	1.5	1.5
Flat-band Potential	non-measurable	0.91	0.95	1.25
Barrier Height	Resistive	1.27	0.99	1.55

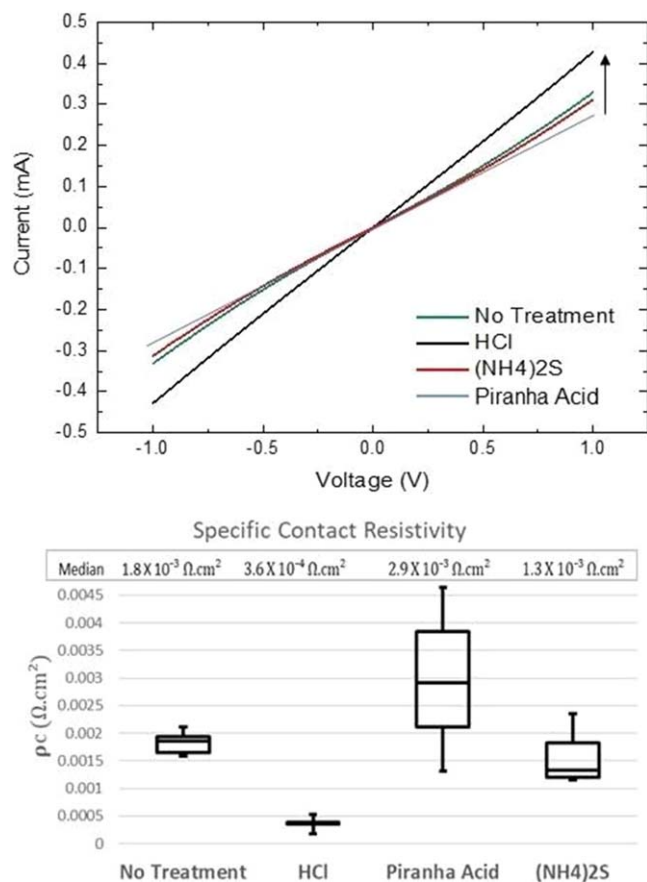
The position of VBM was estimated by taking the intercept at the leading edge of the valence band spectra with the baseline and measuring its distance from the fermi level position (Binding Energy = 0). Figure 6 shows the valence band spectra of the p-GaN after Piranha treatment and approximative band-bending obtained from the position of fermi level from valence band maxima at the surface of p-GaN after different treatments. The distance between the fermi level and V.B.M changes with type of chemical treatment on the surface, indicating the band-bending depends on the surface treatment. The chemical treatment with least band-bending should result in better contact between p-GaN and metal contacts. The p-GaN sample treated with HCl results in highest band-bending whereas Non-treated results in lowest band-bending of 0.81 eV. However, the value of VBM obtained from valence band spectra may get affected by the presence of surface states which have binding energy close to VBM. More surface states present results in more inaccurate VBM analysis.<sup>26</sup> Table II shows the summary of calculated band-bending values, C and O compositions, GaOx percentage and Ga/N ratio. During the surface composition study,

the Ga/N ratio was also calculated. The Ga vacancy/deficiency is considered to be beneficial for p-GaN. The Ga vacancy acts as acceptors resulting in decrease of surface band-bending. The Ga/N ratio of HCl and  $(NH_4)_2S$  was close to stoichiometric ratio of 1, whereas for piranha treatment and non-treated it was  $0.7 \pm 0.1$ . The Ga/N ratio less than 1 indicates N deficiency, which acts as donor for the p-GaN. Taking into account, C contamination, less GaOx percentage, Good Ga/N ratio and less Band-bending  $(NH_4)_2S$  stood out as potential candidate for contact improvement. The HCl treatment also showed least GaOx percentage, stoichiometric Ga/N ratio and can also play important role in contact improvement.<sup>27</sup> The surface morphology and roughness of p-GaN after different chemical treatment was investigated by atomic force microscopy. Depending on the type of chemical treatment prior, the rms surface roughness was different for different sample. An area of  $5 \mu\text{m} \times 5 \mu\text{m}$  scanned to measure the rms roughness of the p-GaN. Figure 7 shows the  $5 \mu\text{m} \times 5 \mu\text{m}$  area morphology image with inset  $1 \mu\text{m} \times 1 \mu\text{m}$  area image of (a) Non-treated (b) HCl (c) Piranha and d.)  $(NH_4)_2S$  respectively. There were particles (white) and holes (black)



**Table II.** Summary of band-bending, GaOx surface composition and Ga/N ratio obtained for p- GaN after different chemical treatment by XPS.

Chemical treatment	Band bending	GaOx percentage	Ga/N ratio	Other impurities
Non-treated	0.81	31%	$0.7 \pm 0.1$	—
HCl	1.1	17%	$1 \pm 0.1$	Cl
Piranha	0.89	42%	0.73	S
$(NH_4)_2 S$	0.87	22%	$1 \pm 0.1$	—

**Figure 9.** I-V Characteristic and specific contact resistivity for non-treated, HCl, piranha and  $(NH_4)_2 S$  treated p-GaN.

present in all the p-GaN samples. The presence of particles with diameter range between 15 nm–180 nm, were may be due to the contaminants on the surface of p-GaN. The presence of holes with diameter between 15 nm–90 nm were may be due to the dislocation terminating at the surface of p-GaN.<sup>28</sup> The shape of these holes were hexagonal, that is typical shape of v-pits formed due to dislocations in p-GaN. The peak-to-valley distance was measured on each sample, the peak-to-valley distance was more for p-GaN samples with more rms roughness. Table III shows the rms roughness and peak-to-valley distance for different treated p-GaN. The p-GaN sample treatment with Piranha gives least rms roughness. The number of particles on Piranha treated p-GaN surface were lesser and larger in diameter as compared to other chemical treated p-GaN. The less surface roughness in piranha treated p-GaN can also be due to passivating impact. HCl treated p-GaN has slightly larger roughness than non-treated due to etching impact of HCl. The surface roughness and surface morphology has impact on the type of contact formation.

The atomic terraces also become more visible after Piranha treated p-GaN. A clean GaN surface has often visible atomic steps/terraces and it forms better contact.<sup>29</sup> This suggests that Piranha treatment resulted in clean p-GaN sample with least roughness.

**Table III.** RMS roughness and Peak-to-Valley distance for different p-GaN sample.

Chemical Treatments	RMS Roughness(nm)	Peak-to-valley(nm)
Non-treated	1.32	50.9
HCl	1.53	66.8
Piranha	0.95	41
$(NH_4)_2 S$	1.85	51

**Electrical measurements.**—After the TLM fabrication the sem image was taken to observe the TLM fabrication and the four-probe electrical characterisation was performed on the linear TLM structure. Figure 8 shows the SEM image of TLM structure after (a) No treatment, (b) HCl, (C) Piranha acid, (d)  $(NH_4)_2 S$  respectively.

The sem image shows that metal contact were properly deposited and there were no photoresist residues. The I–V curve were plotted to see the ohmic and schottky contact formation. Figure 9 shows the I–V curve for Non-treated, HCl, Piranha and  $(NH_4)_2 S$  for smallest contact spacing. The HCl treated p-GaN showed ohmic characteristic with one order of improvement in specific contact compared to other surface treatment. The non-treated, Piranha acid and  $(NH_4)_2 S$  resulted in schottky characteristics. Piranha acid attacks the resist, therefore it was integrated into surface treatment via. Etching method of TLM fabrication. The best contact resistivity achieved were given by HCl treated p-GaN of  $3.6 \times 10^{-4} \Omega \cdot \text{cm}^2$ .

## Conclusions

In conclusion, we demonstrated that HCl treated p-GaN shows improvement in contact which was observed by flatband potential measurement and contact resistivity measurement. The improvement in contact is linked to changes in the surface states and surface alteration of p-GaN after different treatment as confirmed by the detailed electrochemical study and physico-chemical characterisation. The electrochemical study shows that the flatband as well as barrier height and electric circuit model are linked to the surface treatment. The HCl treated surface results in least flatband potential as compared to other chemistry. The XPS characterization shows that HCl results in least gallium oxide percentage on the surface and maintains the stoichiometric ratios on the surface. From XPS test, it was founded that HCl leaves Cl on the surface. These Cl atoms can be beneficial for contact improvement, as shown by TLM electrical tests. Therefore, it can be concluded that the efficient removal of oxides, ideal stoichiometric ratios of Ga and N on surface and Cl impurities are factors contributing to improvement in contact resistivity and ohmic I–V characteristics after HCl treatment.

## Acknowledgments

The authors are thankful to INAC Symmes, CEA and Platform of nanocharacterisation of CEA for their help in electrochemical and physicochemical characterisations. The authors are also grateful to LITP lab of LETI for their contribution in fabrication and test of TLM structures.

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