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# High breakdown voltage GaN Schottky diodes for THz frequency multipliers

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## Abstract

Quasi-vertical gallium nitride (GaN) Schottky diodes on silicon carbide (SiC) substrate were fabricated for frequency multipliers applications. The epitaxial structure employed had a n<sup>-</sup> layer of 590 nm with doping  $6.6 \times 10^{16} \text{ cm}^{-3}$ , while the n<sup>+</sup> layer was 950 nm thick, with doping  $2 \times 10^{19} \text{ cm}^{-3}$ . Potassium hydroxide (KOH) chemical surface treatment before Schottky contact metallization was employed to study its effect in improving the diode parameters. The KOH-treated diode demonstrated a breakdown voltage of -27.5 V, which is the highest reported for this type of diodes. Cut-off frequencies around 500 GHz were obtained at high reverse bias (-25 V) in spite of high series resistance. The result obtained in breakdown voltage value warrants further research in surface treatment and post-annealing of the Schottky contact optimization in order to decrease the series resistance.

**Keywords:** GaN, Schottky diode, frequency multipliers, THz, wide bandgap semiconductor

## 1. Introduction

Terahertz (THz) science has applications in a plethora of multidisciplinary subjects, such as astronomy [1,2], wireless telecommunications [3,4], security [5,6] and biomedical analysis [7]. Numerous recent breakthroughs, as well as recent technological advancements, have moved THz science in the center focus of many researchers by virtue of its wide variety of applications. However, to grow massively, these applications require low cost, compact, portable, reliable and non-cryogenic THz sources and, especially, high power level sources [8]. Frequency multipliers are desirable THz sources thanks to their advantages in terms of performances and cost-efficiency compared to other THz solid-state sources [8,9]. Gallium Nitride (GaN) Schottky diodes have been investigated for frequency multiplier application with increasing interest only in the last few decades. Thus, this technology is far from the completeness of another, more famous, application for which GaN has already proved excellent performances in terms of high power and high frequency electronics: GaN high-electron-mobility transistor (HEMTs) [10]. Nonetheless, the recent push in this research direction for frequency multipliers has been motivated by the possibility of overcoming the intrinsic physical limitations of Gallium Arsenide (GaAs) Schottky diode frequency multipliers [11–14]

Siles et al. [11] demonstrated that, in theory, one GaN Schottky diode multiplier can handle an input power value that is similar to the power injected in a 8 GaAs Schottky diodes multiplier of similar anode area. However, to experimentally demonstrate this appealing result, several challenges have to be overcome. For instance, compared to GaAs, the lower electron mobility of GaN might result in an increased series resistance and, in turn, a generally lower efficiency at high frequencies.

Among the recent progress, C. Jin et al. [15] reported, on sapphire substrate, a GaN Schottky diodes with a cutoff frequency of about 200 GHz at zero bias and 1.2 THz at -8 V, on sapphire substrate. On a similar substrate, Liang et al. [16] reported a cutoff frequency of 902 GHz for a GaN diode with an anode diameter of 2  $\mu\text{m}$  and more recently, a GaN Schottky diode on silicon carbide (SiC) substrate with cutoff frequency of 459 GHz (with anode diameter of 5  $\mu\text{m}$ ) [17].

In this work, quasi-vertical GaN Schottky diodes on SiC substrate are fabricated and characterized, investigating the effect of KOH surface treatment before Schottky contact metallization on the breakdown voltage ( $V_{BD}$ ), diode parameters, and extracted cutoff frequency.

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## 2. Device fabrication

The GaN Schottky diode epitaxial layer used in this study was grown by metal organic vapor phase epitaxy (MOVPE) on semi-insulating 6H-SiC substrate and is shown in *Figure 1*. A 490 nm unintentionally doped GaN was grown on top of a 300 nm AlN nucleation layer. Then, two highly doped  $n^+$  GaN layers, respectively 950 nm thick ( $2 \times 10^{19} \text{ cm}^{-3}$ ) and 300 nm thick ( $1 \times 10^{19} \text{ cm}^{-3}$ ) were grown to achieve low ohmic contact and series resistance and 590 nm  $n^-$  GaN ( $6.6 \times 10^{16} \text{ cm}^{-3}$ ) acted as the Schottky layer. This process was first optimized on sapphire substrate [18] and then adapted for SiC substrate technology.

590 nm $n^-$ GaN $6.6 \cdot 10^{16} \text{ cm}^{-3}$
650 nm $n^+$ GaN $2 \cdot 10^{19} \text{ cm}^{-3}$
300 nm $n^+$ GaN $1 \cdot 10^{19} \text{ cm}^{-3}$
490 nm u-GaN
300 nm AlN
6H-SiC

*Figure 1. Schematic view of the GaN on SiC epitaxial structure employed in this study*

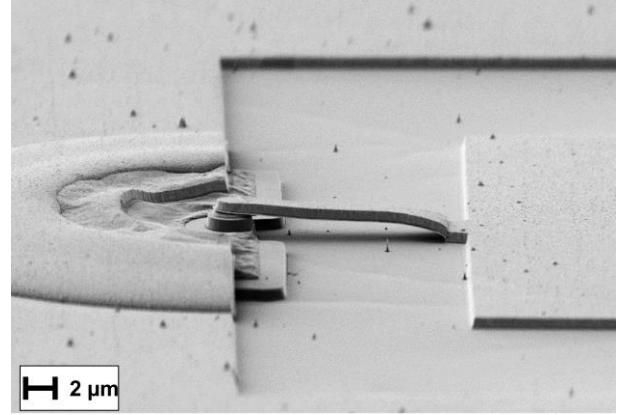
All the lithographic steps were performed through e-beam lithography. The diode mesa was defined by etching the  $n^-$  layer down to the  $n^+$  layer with  $\text{Cl}_2$ -based inductively coupled plasma (ICP) dry etching. Then, a multilayer of Ti/Al/Ni/Au was evaporated onto the sample for ohmic contact annealed at  $850^\circ \text{C}$  for 30 s. The contact was fabricated with standard lift-off technique. Before Schottky contact metallization, potassium hydroxide (KOH) chemical surface treatment (50%, at  $80^\circ \text{C}$  for 1 min) was applied to investigate its effect on the diode performances. A bilayer of Pt/Au was evaporated on the  $n^-$  layer as Schottky contact, which was then annealed at  $400^\circ \text{C}$  for 5 min.

After Schottky metallization, the diodes were isolated through  $\text{Cl}_2/\text{Ar}$  ICP etching of the  $n^+$  layer down to the resistive buffer. The last step consisted in the lithography and metallization of the air-bridge and the metal pads for coplanar access. *Figure 2* shows a fabricated diode with a diameter of about  $2 \mu\text{m}$ .

## 3. Results and discussion

### 3.1 Physical characterization

SiC substrate presents several advantages for GaN heteroepitaxy, when compared to other commonly used substrates like silicon or sapphire [19], such as a smaller lattice constant mismatch (3.1%) and a higher thermal conductivity ( $3.8 \text{ W cm}^{-1} \text{ K}$ ) [20]. Another strong point is the



*Figure 2. GaN Schottky diode with air-bridge structure*

possibility of making the SiC substrate conductive, unlike sapphire for instance, thus allowing the use of simplified device architectures. Nonetheless, this heteroepitaxial technology suffers from issues, such as an increased resistance between the device and the substrate due to the use of buffer layers during the growth process. Moreover, the low lattice mismatch is still sufficient to produce large density of defects. The screw dislocation density in SiC is typically around  $10^3 - 10^4 \text{ cm}^{-2}$  [21].

A chemical surface treatment applied before Schottky contact metallization can remove contaminants from the semiconductor surface [22], and a post-annealing of the Schottky contact can promote a structural reorganization at the metal/semiconductor interface, thus reordering the lattice structure in its most stable configuration [23], and these two techniques may improve the Schottky diode parameters, on a given GaN epitaxy.

The KOH chemical surface treatment was, in fact, applied in the optics of minimizing the non-idealities that could stem from the various defects present in the GaN epitaxial layers. The physical characterization was carried out with atomic force microscope (AFM) scans and X-ray photoelectron spectrometry (XPS) analysis.

*Figure 3* shows AFM scans of randomly selected areas of  $5 \times 5 \mu\text{m}$ . The untreated sample (reference) was characterized by a root mean squared (rms) surface roughness of  $0.266 \text{ nm}$ , while the rms surface roughness of the KOH-treated sample was  $0.404 \text{ nm}$ .

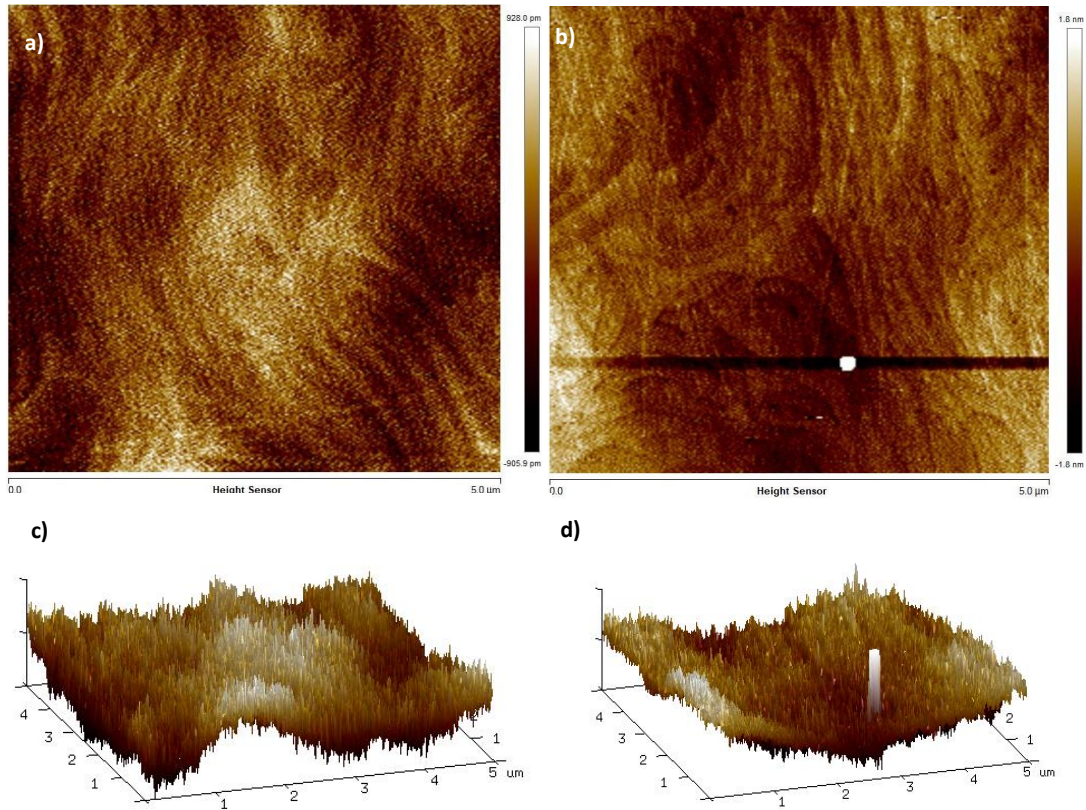


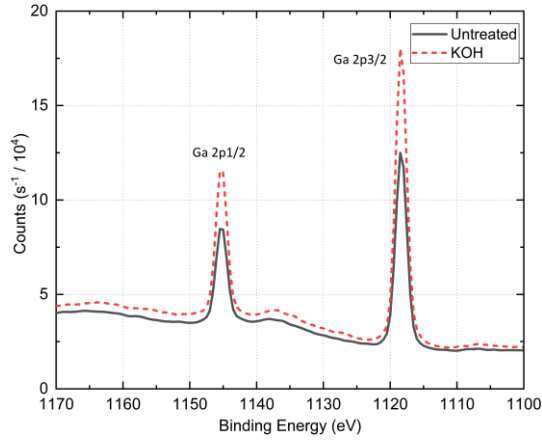
Figure 3. 5x5  $\mu\text{m}$  AFM scans of GaN on SiC: untreated sample ((a) and (c)), and KOH-treated sample ((b) and (d))

Typical XPS spectra are presented in Figure 4a and b whereas the quantitative analysis results are gathered in Table I, where the intensity ratios have been corrected for elemental sensitivity factors [24]. It reveals that the KOH treatment is effective in decreasing both C and O surface contamination, which results in an increase of the  $\text{N}_{1s}/\text{Ga}_{3d}$  intensity ratio. The KOH treatment is also responsible for the presence of some trace of K on the semiconductor surface (as seen in Figure 4b), similarly to other type of treatments, such as HCl and HF, that are also effective in decreasing native contaminations, however introducing, respectively, Cl and F contaminants [22,25–27].

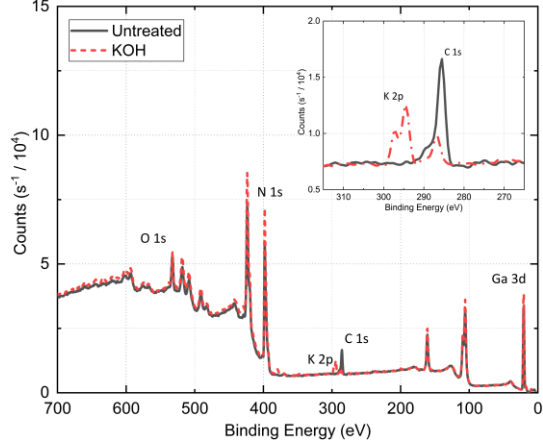
In their study of KOH treatment on the surface of n-GaN, Moldovan et al. [28] found that the treatment produced an increase of N and a decrease of Ga surface content, as well as a decrease of C contamination, while the binding energy of the  $\text{O}_{1s}$  peaks remained unchanged. Our findings are clearly in line with their results. Rickert et al. [29] demonstrated that the KOH treatment was responsible for a shift of the  $\text{Ga}_{3d}$  peak of about 0.3 eV toward lower binding energy, corresponding to a shift of the surface Fermi level closer to the valence band maximum [30], which in turns could result

in an increased contact resistance. We did not observe such a shift in  $\text{Ga}_{3d}$  binding energy. Ultimately, they concluded that the KOH treatment removes Ga content from the surface due to the formation and dissolution of Ga-based hydroxide [31], thus decreasing the  $\text{Ga}/\text{N}$  ratio.

Since understanding the state of the surface of a semiconductor is one of the most critical steps of a Schottky diode fabrication process, in the next section the electrical characterization results will be analyzed also in correlation to the physical changes observed in this section, in order to



a) Ga 2p lines



b) Other XPS lines

Figure 4. XPS survey spectra for Ga (a), N and other notable lines (b)

establish a cause-effect relationship between the surface chemical treatment and the Schottky diode behavior.

Sample	$N_{1s}/Ga_{3d}$	$C_{1s}/Ga_{3d}$	$O_{1s}/Ga_{3d}$
Untreated	0.868	0.429	0.261
KOH	1.040	0.081	0.180

Table I. Quantitative analysis of elemental intensities

### 3.2 DC Characterization

DC characterization was performed with an Agilent E5263A 2 Channel IV Analyzer/Source monitor unit. Schottky contact annealing resulted to be mandatory to improve the Schottky diode parameters and reduce leakage current under reverse bias.

The analyzed diodes have, for both surface treatments, a diameter of 6  $\mu m$ .

Figure 5 shows the DC characteristics of the Schottky diodes. The untreated GaN diode was characterized by a barrier height of 0.52 eV, an ideality factor of 1.55, and an extracted series resistance of 34.61  $\Omega$ , while the KOH-treated diode yielded a barrier height of 0.53 eV, an ideality factor of 1.28, and a series resistance of 31.18  $\Omega$ . The study of the reverse I-V characteristics showed a breakdown voltage at 1  $\mu A$  of  $-19.3 V$  and  $-27.5 V$ , respectively for the untreated and the KOH-treated diode. The parameters are summarized in Table II. Reported values of the breakdown voltage of GaN Schottky diodes for frequency multipliers in the recent literature are  $-19.5 V$  (for diodes with anode diameter of 6.5 and 4.5  $\mu m$ ) [32],  $-15.4 V$  (5  $\mu m$ ) [17], both for SiC substrate, and  $-12 V$  (2  $\mu m$ ) for sapphire substrate [16]. When developing a GaN Schottky diode for frequency multipliers, the first figure of merit is its breakdown voltage. The diodes presented in this work show desirable breakdown

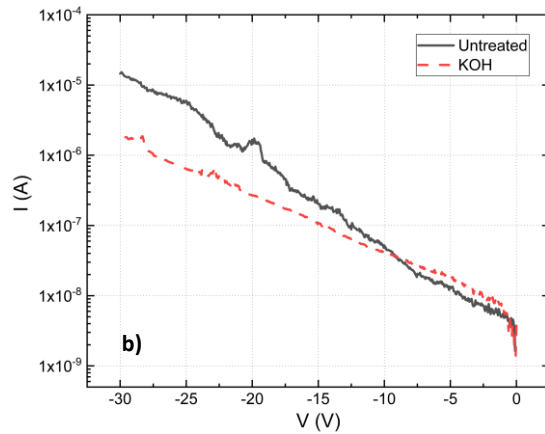
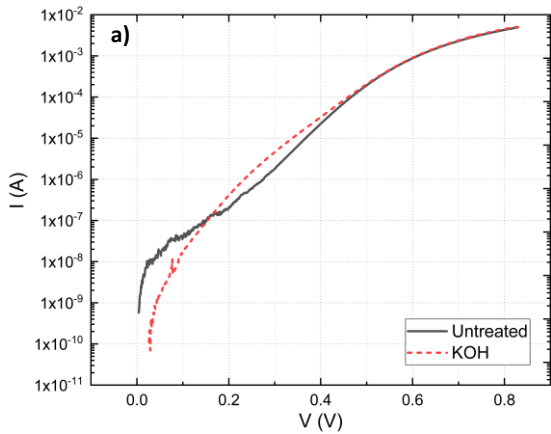


Figure 5. DC forward (a) and reverse (b) characteristics for the GaN on SiC Schottky diodes



voltages, comparable to the state of the art in the case of the untreated diode, and significantly higher in the case of the KOH-treated diode.

	Untreated	KOH
$\phi_B$ (eV)	0.52	0.53
$n$	1.55	1.28
$R_S$ ( $\Omega$ )	34.61	31.18
$V_{BD}$ @ $1\mu\text{A}$ (V)	-19.3	-27.5

Table II. Schottky diode parameters extracted from DC characterization

The KOH chemical surface treatment does not seem to have a significant impact on the other diode parameters, save for a slight improvement of the ideality factor. The ideality factor is an empirical rule of thumb to indicate the grade of deviation of a Schottky diode I-V characteristics from pure thermionic emission (TE). The ideal case corresponds to  $n = 1$ . A higher than unity ideality factor typically indicates the presence of one or more current conduction mechanisms other than TE. Tunneling [33] and/or generation/recombination current, image-force lowering [34], interface states [35] are all elements that contribute to the increase of the ideality factor.

The lower ideality factor observed for the KOH-treated diode might be explained by the removal of native surface contaminants during the chemical treatment itself, as shown in the XPS analysis. This type of improvement is evident when looking at the value of the breakdown voltage and at the behavior of the reverse characteristics in Figure 5b, which shows a clear reduction in leakage current. Moreover, this is further supported by the minor decrease in series resistance. A similar treatment in [36], performed on GaN on sapphire Schottky diodes, reported as well a reduction of leakage current after KOH treatment, associated to a general improvement of the diode rectifying characteristics.

It is worth noting that the KOH treatment induced an increase in surface roughness, although this did not seem detrimental to the diode parameters. A number of works in the literature [28,29] attest that KOH may be able to etch GaN under certain conditions, although a direct comparison is not possible due to the spread and heterogeneity of the chemical treatments conditions, and, most of all, the differences in the heteroepitaxial GaN used. Actually, growth conditions, type of substrate used, doping level and epitaxial layer thickness are all factors that vary in each work reported in the literature, thus making extremely difficult a direct comparison of results and performances.

### 3.3 Small-signal high frequency characterization

On-wafer small-signal S-parameter measurements were carried out between 250 MHz and 67 GHz with an Agilent E8361A PNA network analyzer. After de-embedding [37], the total capacitance was extracted using the imaginary part of  $Y_{12}$ , through the model detailed in [38]. An example can be seen in Figure 6, where the extracted total capacitance for the KOH-treated diode is shown.

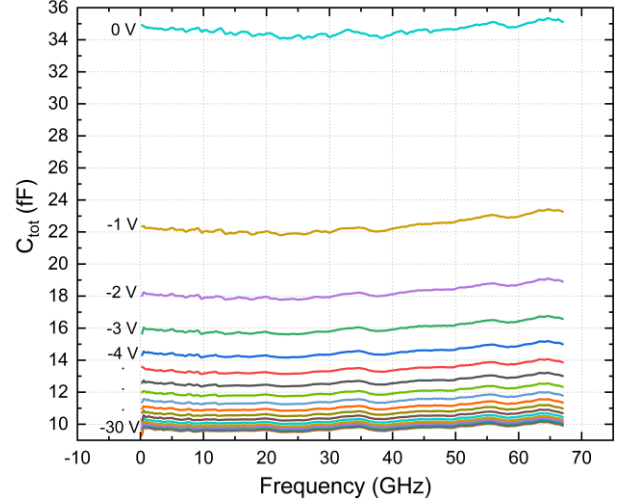


Figure 6. Total capacitance as extracted from de-embedded S-parameter measurements of the KOH-treated  $6\mu\text{m}$  GaN Schottky diode for each bias point (starting from 0V with the top curve and going down to -30V, with step of -1V)

Rather than choosing a single frequency to extract the capacitance, a statistical analysis was performed between 10 and 30 GHz to extract an average value. The standard deviation was used to characterize the validity of this statistic, and was found to be at least three orders of magnitude lower than the average value. The zero-bias junction capacitance  $C_{j0}$  was obtained with a non-linear fit of the total capacitance values at each bias point with

$$C_{tot}(V) = C_{j0} \left(1 - \frac{V}{V_{bi}}\right)^{-0.5} + C_{par} \quad (1)$$

The series resistance  $R_S$  was calculated in an analogous way from the real part of  $Y_{12}$  in the forward bias region, and compared to the value extracted from DC measurements. The cutoff frequency was calculated with the extracted values of  $C_{j0}$  and  $R_S$ . The obtained diode parameters are reported in Table III, and the cutoff frequencies are illustrated in Figure 7.

	Untreated	KOH
$V_{BD} @ 1\mu A$ (V)	-19.3	-27.5
$C_{j0}$ (fF)	27.3	30
$R_s$ ( $\Omega$ )	34.7	33.3
$f_{c0}$ (GHz)	168.2	159.4

Table III. Schottky diode parameters extracted from high frequency characterization

At zero bias, the cutoff frequency is 168 GHz and 159 GHz, respectively for the untreated and for the KOH-treated diode. When compared to the values of the literature, such as 459 GHz [17], the cutoff frequencies extracted in this work are relatively low, owing to a (relatively) high series resistance. In fact, this is one of the bottleneck of GaN as a substitute material for GaAs in frequency multiplier technology relying on Schottky diodes [12].

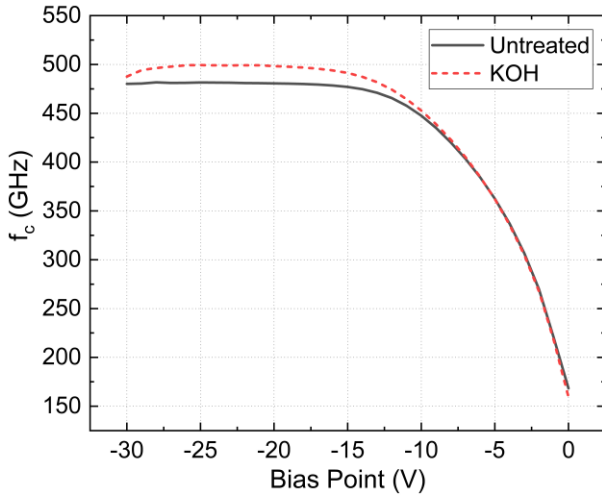


Figure 7. Calculated cut-off frequency for the analysed diodes

#### 4. Conclusions

In summary, quasi-vertical GaN Schottky diodes were fabricated on n-type GaN on SiC substrate. A KOH chemical treatment was applied to the semiconductor surface before Schottky contact metallization to investigate its effect on the diode characteristics and parameters. The breakdown voltages obtained were -19.3 V and -27.5 V at 1  $\mu A$  respectively for the untreated and the KOH-treated diode. The breakdown voltage obtained with the KOH-treated diode is significantly higher than the current state of the art (-19.5 V). This improvement was associated to a reduction of the diode leakage current, and a general improvement of the diode rectifying characteristics. The obtained cutoff frequencies at zero bias were 168 GHz and 159 GHz, for the untreated and KOH-treated diode, respectively. These values are lower than the current state of the art because of the high

series resistance of the diodes. However, the very promising result obtained in breakdown voltage is sufficient to push continued research in the optimization of the semiconductor surface treatment oriented towards the improvement of the diode parameters for its final application: THz GaN based multipliers enabling high frequency and high-power operation.

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#### Conflict of interest

The authors declare no conflict of interest.

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