# High Density Plasma Damage Induced in n-GaN Schottky Diodes Using Cl<sub>2</sub>/Ar Discharges

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### ABSTRACT

The effects of dc chuck self-bias and high density source power (which predominantly control ion energy and ion flux, respectively) on the electrical properties of n-GaN Schottky diodes exposed to Inductively Coupled Plasma of Cl<sub>2</sub>/Ar were examined. Both parameters were found to influence the diode performance, by reducing the reverse breakdown voltage and Schottky barrier height. All plasma conditions were found to produce a nitrogen-deficient surface, with a typical depth of the non-stoichiometry being ~500 Å. Post-etch annealing was found to partially restore the diode characteristics.

#### INTRODUCTION

There is a strong interest in GaN-based electronics for high power, high temperature applications in communications, power switching and microwave amplifiers [1-9]. There have been impressive reports of high performance GaN/AlGaN heterostructure field effect transistors [2-9] grown on Al<sub>2</sub>O<sub>3</sub> or SiC substrates. Other prototype devices include a depletion-mode GaN MOSFET [10], GaN/AlGaN heterostructure bipolar transistors [11-13] and GaN rectifiers [14] and junction field effect transistors [15]. Precise pattern transfer during fabrication of these devices requires use of dry etching methods with relatively high ion energy in order to break the strong Ga-N bonds (8.92eV/atom) [16]. Under those conditions there will generally be some ion-induced damage remaining in the GaN after dry etching, along with the possibility of a non-stoichiometric near–surface region due to preferential loss of atomic nitrogen in the form of N<sub>2</sub> [17-19]. The Ga etch product in Cl<sub>2</sub>-based discharges is GaCl<sub>3</sub>, and this is less volatile than N<sub>2</sub> both from a pure chemical vapor presence and from a preferential sputtering viewpoint.

There is a clear need to better understand the role of plasma exposure on the resultant electrical performance of GaN-based devices, both from an etching and deposition viewpoint. Exposure to pure Ar discharges was found to produce higher reverse bias leakage currents in p-n junction structures compared to use of  $Ar/N_2$  discharges [20]. Even relatively low power reactive ion etching (RIE) conditions were found to deteriorate the quality of Schottky contacts deposited on plasma-etched n-GaN [21, 22]. The preferential loss of nitrogen from the GaN surface does improve the specific contact resistance of n-type ohmic contacts because of the creation of a degenerately doped surface layer [23].

In this work we have examined the effect of Inductively Coupled Plasma (ICP) on

the reverse breakdown voltage ( $V_B$ ), Schottky barrier height ( $\varphi_B$ ) and forward turn-on voltage of ( $V_F$ ) of GaN diode rectifiers with the contacts already in place. Several methods for damage removal were investigated, including annealing, UV ozone oxidation/stripping or wet etching with NaOH solutions.

### EXPERIMENTAL

The diodes were fabricated on nominally undoped  $(n\sim10^{17} \text{ cm}^{-3})$  or Si-doped  $(5\times10^{17} \text{ cm}^{-3})$  GaN layers  $\sim 3\mu$ m thick grown on an n<sup>+</sup>(10<sup>18</sup> cm<sup>-3</sup>) GaN buffer on c-plane Al<sub>2</sub>O<sub>3</sub> substrate. Ohmic contacts were formed with lift-off Ti/Au subsequently annealed at 600 °C, followed by evaporation of the 250  $\mu$ m diameter Pt(250Å)/Au(1500Å) Schottky contacts through a stencil mask. A schematic is shown in Figure 1. The samples were briefly exposed (~10secs controlled by the system software) to 10Cl<sub>2</sub>/5Ar (total gas load 15 standard cubic centimeters per minute) or 15Ar ICP discharges in a Plasma Therm 790 reactor. During the ignition stage of discharge, the dc self-bias takes ~2secs to reach its final value. Longer exposure time resulted in more damage. Damage layer thickness was limited due to Cl<sub>2</sub>/Ar etching of damaged GaN at a rate of around 1000 Å/min. From limited measurements we found that damage depth saturates in 10secs (~500Å). The gases were injected directly into the source through electronic mass flow controllers, and the 2MHz source power was varied from 100-1000 W. The samples were placed on an rf-powered (13.56MHz, 5-300W), He backside-cooled chuck. Process pressure was held constant at 2 m Torr.

Ti/Au	Ni/Pt	Ti/Au
$3\mu m$ undoped (n~ $10^{17}$ cm <sup>-3</sup> ) GaN		
$0.3 \ \mu m \ n^+ \ (10^{18} \ cm^{-3}) \ GaN$		
Al <sub>2</sub> O <sub>3</sub> substrate		

Figure 1. Schematic of the planar diodes

# **RESULTS AND DISCUSSION**

The dependence of  $V_B$  and  $\dot{\varphi}_B$  on rf chuck power for 300W source power discharges is shown in the upper part of Figure 2. Both of these parameters, at least initially, decrease with increasing power. The  $\dot{\varphi}_B$  values saturate beyond 50W. The main effect on  $\dot{\varphi}_B$  is from damage created around the contact periphery. This would expected to saturate once a N<sub>2</sub>-deficient region is created because much of the resultant  $\dot{\varphi}_B$  is still determined by the unexposed region under the contact metal. Under these conditions, the dc chuck self-bias increases from -105 V at 50 W to -275 V at 200 W. The average ion energy is roughly the sum of this voltage plus the plasma potential which is 20-25 V in this system under these conditions. After plasma exposure, the diode ideality factor was always ≥2 (the reference ideality factor was ~1.3), which is a further indication of the degradation in electrical properties of the structures. The results are consistent with creation of an ion damaged, non-stoichiometric GaN surface region. This region exists in the plasmaexposed area outside the metal contacts. Note that the GaN etch rate increases monotonically with rf chuck power (lower part of the Figure 2), but this more rapid removal of material is not enough to offset the greater amount of damage caused by the higher-energy ion bombardment. We believe the GaN must be non-stoichiometric and hence more n-type at the surface because of the sharp decreases observed in V<sub>B</sub>. In the case of compound semiconductors with less bond energy the damage may induce into the bulk materials and the defect may traps the carriers. For GaAs where ion bombardment creates more resistive material by introduction of deep compensating levels rather than shallow donor states, the breakdown voltage is generally found to increase with exposure to plasmas.

The dependence of  $V_B$  and  $\phi_B$  on ICP source power is shown in Figure 3 (top).

While  $\phi_B$  continues to decrease as the ion flux increases,  $V_B$  initially degrades but shows less of a decrease at higher source powers. This is most likely a result of the continued decrease in the self-bias at higher source power. This also leads to a decrease in GaN etch rate above 500 W. The results of Figure 2 and 3 show that both ion energy and ion flux are important in determining not only the GaN etch rate, but also the amount of residual damage in the diodes.

To establish the chemical state of the GaN surface at different stages, AES was performed on an unmetallized sample. Figure 4 shows surface scans before (top) and after (lower) exposure to a 500 W source power, 50 W chuck power  $Cl_2$ /Ar discharge.



**Figure 2.** *rf chuck power dependence of*  $V_B$  *and*  $\phi_B$  *in*  $Cl_2/Ar$  *plasma exposed GaN diodes (top) and of dc chuck self-bias and GaN etch rate under the same conditions (bottom).* 



**Figure 3** ICP power dependence of  $V_B$  and  $\phi_B$  in Cl<sub>2</sub>/Ar plasma exposed GaN diodes (top) and of dc chuck self-bias and GaN etch rate under the same conditions (bottom).

The main change is a reduction in the  $N_2$  signal in the latter sample (by ~20%), confirming

the preferential loss of this element during dry etching. Subsequent annealing at 700  $^{\circ}$ C in N<sub>2</sub> restored some of this deficiency (Figure 4, bottom).

We also examined the use of wet etch removal of the damaged region with hot NaOH solutions (0.1M, 80 °C). This was found to be successful in etching the damaged GaN and was self-limiting in that once the undamaged material was reached, the etching stopped. We typically found a damage depth of ~500Å. The wet etching usually can restore >70% of the original V<sub>B</sub>. The use of UV ozone oxidation followed by stripping of the oxide also produced some improvement in diode characteristics (typically ~50% of the original V<sub>B</sub> was restored), but each cycle removes only ~30Å, and thus 15-20 cycles would be needed to completely restore the initial properties.

## SUMMARY AND CONCLUSIONS

We found that ICP  $Cl_2$ /Ar discharges degrade the performance of GaN Schottky diodes, with ion energy and ion flux both playing important roles. The degradation mechanism appears to be creation of a conducting, non-stoichiometric (N<sub>2</sub>-deficient) near-surface region on the GaN. While UV ozone oxidation of the surface and subsequent dissolution of the oxidized region in HCl provides some restoration of the electrical

properties of the GaN, etching in NaOH or annealing at 700 - 750 °C may restore most of the initial reverse breakdown voltage characteristics.



**Figure 4.** AES surface scans from GaN (top) or after (center) Cl<sub>2</sub>/Ar plasma exposure, and subsequent annealing at 700 <sup>c</sup>C for 60 seconds (bottom).

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