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Plasma Damage in p-GaN

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Abstract

The effect of Inductively Coupled Plasma H_2 or Ar discharges on the breakdown voltage of p-GaN diodes was measured over a range of ion energies and fluxes. The main effect of plasma exposure is a decrease in net acceptor concentration to depths of 400-550Å. At high ion fluxes or energies there can be type conversion of the initially p-GaN surface. Post etch annealing at 900°C restores the initial conductivity.

Introduction

Understanding the effects of plasma-induced damage in GaN has become more important as the interest in electronic devices for high temperature, high power applications has increased. One clear example is in the fabrication of GaN/AlGaN heterojunction bipolar transistors (HBTs)[1-3] or GaN bipolar junction transistors (BJTs)[4] where it is necessary to etch down to both a p-type base layer and an n-type subcollector layer. Energetic ion damage may result in increased surface and bulk leakage currents and changes in the electrical properties of the near-surface region through a change in Ga/N stoichiometry.[5] In other compound semiconductor systems it is often possible to remove plasma-damaged regions using slow wet chemical etching.[6] In the GaN system, much less is known about the electrical effects of dry etch damage, and its subsequent removal by wet etching or annealing.

Most past work in this area has focussed on n-type material. The sheet resistances of GaN[7], InGaN[8], InAlN[8] and InN[8] samples were found to increase in proportion to ion flux and ion energy in an Electron Cyclotron Resonance (ECR) Ar plasma. Ren et.al.[9,10] examined the effect of ECR BCl_3/N_2 and CH_4/H_2 plasmas on the electrical performance of InAlN and GaN channel field effect transistors. They found that hydrogen passivation of the Si doping in the channel may occur if H_2 is a part of the plasma chemistry and that preferential loss of N_2 degraded the rectifying properties of Schottky contacts deposited on plasma-exposed surfaces. Ping et.al.[11,12] found more degradation in GaN Schottky contacts exposed to Ar plasmas relative to $SiCl_4$ exposure, which would be expected on the basis of the faster etch rate with the latter and hence improved damage removal. In general it is found that ion damage tends to increase the n-type doping level at the surface, most likely through preferential loss of N_2, and that the bandedge photoluminescence intensity decreases through introduction of non-radiative levels.[13-17]

Shul et.al.[5] reported that the sheet resistance of p-GaN increased upon exposure to Inductively Coupled Plasmas (ICP) of pure Ar. The increases were almost linearly dependent on ion energy (90% increase at –350eV), but weakly dependent on ion flux (~25% increase at $\sim 10^{17}$ ions $\cdot$ $cm^{-2} \cdot s^{-1}$).

In this paper we report a systematic study of the effects of ICP H_2 or Ar damage on the breakdown voltage of p-GaN Schottky diodes. We find there is surface conversion of the p-type GaN at high ion fluxes or energies. The depth of the damaged region is 400-500Å and the electrical properties can be essentially restored by annealing in the range 800-900°C.

Experimental

The layer structure consisted of 1μm of undoped GaN ($n \sim 5 \times 10^{16}$ cm^{-3}) grown on a c-plane Al_2O_3 substrate, followed by 0.3 μm of Mg doped ($p \sim 10^{17}$ cm^{-3}) GaN. The samples were grown by rf plasma-assisted Molecular Beam Epitaxy.[8] Ohmic contacts were formed with Ni/Au deposited by e-beam evaporation, followed by lift-off and annealing at 750°C. The GaN surface was then exposed for 1 min to ICP H_2 or Ar plasmas in a Plasma-Therm 790 System. The 2MHz ICP source power was varied from 300-1400 W, while the 13.56 MHz rf chuck power was varied from 20-250 W. The former parameter controls ion flux incident on the sample, while the latter controls the average ion energy. Prior to deposition of 250μm diameter Ti/Pt/Au contacts through a stencil mask, the plasma exposed surfaces were either annealed under N_2 in a rapid thermal annealing system, or immersed in boiling NaOH solutions to remove part of the surface. As reported previously it is possible to etch damaged GaN in a self-limiting fashion in hot alkali or acid solutions.[19-21] The current-voltage (I-V) characteristics of the diodes were recorded on an HP 4145A parameter analyzer. A schematic of the final test structures is shown in Figure 1. The unetched control diodes have reverse breakdown voltages of ~2.5-4 V depending on the wafer – these values were uniform (±12%) across a particular wafer.

Results and Discussion

Figure 2 shows the I-V characteristics from samples exposed to either H_2 (top) or Ar (bottom) ICP discharges (150 W rf chuck, 2 mTorr) as a function of source power. In both cases there is an increase in both the reverse breakdown voltage and the forward turn-on voltage, with these parameters increasing monotonically with the source power during plasma exposure.

Figure 3 shows this increase in breakdown voltage as a function of source power, and also the variation of the chuck dc self-bias. As the source power increases, the ion density also increases and the higher plasma conductivity suppresses the developed dc bias. Note that the breakdown voltage of the diodes continues to increase even as this bias (and hence ion energy, which is the sum of this bias and the plasma potential) decreases. These results show that ion flux plays an important role in the change of diode electrical properties. The other key result is that Ar leads to consistently more of an increase in breakdown voltage, indicating that ion mass is important rather than any chemical effect related to removal of N_2 or NH_3 in the H_2 discharges.

The increase in breakdown voltage on the p-GaN is due to a decrease in hole concentration in the near-surface region through the creation of shallow donor states. The key question is whether there is actually conversion to an n-type surface under any of the plasma conditions. Figure 4 shows the forward turn-on characteristics of the p-GaN diodes exposed to different source power Ar discharge at low source power (300 W), the turn-on remains close to that of the unexposed control sample However there is a clear increase in the turn-on voltage at higher source powers, and in fact at ≥750 W the characteristics are those of an n-p junction.[22] Under these conditions the concentration of plasma-induced shallow donors exceeds the hole concentration and there is surface conversion. In other words the metal-p GaN diode has become a metal-n GaN-p GaN junction. We always find that plasma exposed GaN surfaces are N_2-deficient relative to their unexposed state[5,8,9,10,15], and therefore the obvious conclusion is nitrogen vacancies create shallow donor levels. This is consistent with thermal annealing experiments in which N_2 loss from the surface produced increased n-type conduction.[23,24]

The influence of rf chuck power on the diode I-V characteristics is shown in Figure 5 for both H_2 and Ar discharges at fixed source power (500 W). A similar trend is observed as for the source power experiments, namely the reverse breakdown voltage increases, consistent with a reduction in p-doping level near the GaN surface.

Figure 6 plots breakdown voltage and dc chuck self-bias as a function of the applied rf chuck power. The breakdown voltage initially increases rapidly with ion energy (the self bias plus ~25 V plasma potential) and saturates above ~100 W probably due to the fact that sputtering yield increases and some of the damaged region is removed. Note that these are very large changes in breakdown voltage even for low ion energies, emphasizing the need to carefully control both flux and energy. We should also point out that our experiments represent worse-case scenarios because with real etching plasma chemistries such as Cl_2/Ar, the damaged region would be much shallower due to the much higher etch rate. As an example, the sputter rate of GaN in a 300 W source power, 40 W rf chuck power Ar ICP discharge in ~40Å·min^{-1}, while the etch rate in a Cl_2/Ar discharge under the same conditions is ~1100Å·min^{-1}.

An important question is the depth of the plasma-induced damage. We found we were able to etch p-GaN very slowly in boiling NaOH solutions, at rates that depended on the solution molarity (Figure 7) even without any plasma exposure of the material. This enabled us to directly measure the damage depth in plasma exposed samples in two different ways.

The first method involved measuring the etch rate as a function of depth from the surface. Defective GaN resulting from plasma, thermal or implant damage can be wet chemically etched at rates much faster than undamaged material because the acid or base solutions are able to attack the broken or strained bonds present. Figure 8 shows the GaN etch rate as a function of depth in samples exposed to a 750 W source power, 150 W rf chuck power Ar discharge. The etch rate is a strong function of the depth from the surface and saturates between ~425-550Å. Within this depth range the etch rate is returned to the "bulk" value characteristic of undamaged p-GaN.

The second method to establish damage depth of course is simply to measure the I-V characteristics after removing different amounts of material by wet etching prior to deposition of the rectifying contact. Figure 9 (top) shows the I-V characteristics from samples exposed to 750 W source power, 150 W rf chuck power (-160 V dc chuck bias) Ar discharges and subsequently wet etched to different depths using 0.1 M NaOH solutions before deposition of the Ti/Pt/Au contact. Figure 9 (bottom) shows the effect of the amount of material removed on the diode breakdown voltage. Within the experimental error of ± 12%, the initial breakdown voltage is re-established in the range 400-450Å. This is consistent with the depth obtained from the etch rate experiments described above. These values are also consistent with the damage depths we established in n-GaN diodes exposed to similar plasma conditions.[25]

The other method of removing plasma-induced damage is annealing. In these experiments we exposed the samples to the same type of plasma (Ar, 750 W source power, 150

W rf chuck power) and then annealed under N_2 at different temperatures. Figure 10 (top) shows the I-V characteristics of these different samples, while Figure 10 (bottom) shows the resulting breakdown voltages as a function of annealing temperature. On this wafer, plasma exposure caused an increase in breakdown voltage from ~2.5 to ~18 V. Subsequent annealing at 400°C initially decreased the breakdown voltage, but higher temperature produced a large increase. At temperatures above 700°C, the diodes characteristics returned toward their initial values and were back to the control values by 900°C. This behavior is similar to that observed in implant-isolated compound semiconductors where ion damage compensates the initial doping in the material, producing higher sheet resistances.[26] In many instances the damage site density is larger than that needed to trap all of the free carriers, and trapped electrons or holes may move by hopping conduction. Annealing at higher temperatures removes some of the damage sites, but there are still enough to trap all the conduction electrons/holes. Under these conditions the hopping conduction is reduced and the sample sheet resistance actually increases. At still higher annealing temperatures, the trap density falls below the conduction electron or hole concentration and the latter are returned to their respective bands. Under these conditions the sample sheet resistance returns to its pre-implanted value. The difference in the plasma exposed samples is that the incident ion energy is a few hundred eV compared to a few hundred keV in implant-isolated material. In the former case the main electrically active defects produced are nitrogen vacancies near the surface, whereas in the latter case there will be vacancy and interstitial complexes produced in far greater numbers to far greater depths. In our previous work on plasma damage in n-GaN we found that annealing at ~750°C almost returned the electrical properties to their initial values.[25] If the same defects are present in both n- and p-type material after plasma exposure, this difference in annealing temperature may be a result of a Fermi level dependence to the annealing mechanism.

Summary and Conclusions

The main conclusions of this study may be summarized as follows:

1. The effect of either H_2 or Ar plasma exposure on p-GaN surfaces is to decrease the net acceptor concentration through creation of shallow donor levels, most likely N_V. At high ion fluxes or ion energies there can be type conversion of the initially p-type surface. The change in electrical properties is more pronounced with Ar than with H_2 plasmas under the same conditions.

2. Two different techniques for measuring the damage depth find it to be in the range 400-550Å under our conditions. After removing this amount of GaN, both the breakdown voltage and wet chemical etch rates are returned to their initial values.

3. Post-etch annealing in N_2 at 900°C restores the initial breakdown voltage on plasma exposed p-GaN. Annealing at higher temperatures degraded the electrical properties, again most likely due to N_2 loss from the surface.

Acknowledgments

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Figure Captions

Figure 1. Schematic of p-GaN Schottky diode structures.

Figure 2. I-V characteristics from samples exposed to either H_2 (top) or Ar (bottom) ICP discharges (150W rf chuck power) as a function of ICP source power prior to deposition of the Ti/Pt/Au contact.

Figure 3. Variation of diode breakdown voltage in samples exposed to H_2 or Ar ICP discharges (150 W rf chuck power) at different ICP source powers prior to deposition of the Ti/Pt/Au contact. The dc chuck self-bias during plasma exposure is also shown.

Figure 4. Forward turn-on characteristics of diodes exposed to ICP Ar discharges (150 W rf chuck power) at different ICP source powers prior to deposition of the Ti/Pt/Au contact.

Figure 5. I-V characteristics from samples exposed to either H_2 (top) or Ar (bottom) ICP discharges (500W source power) as a function of rf chuck power prior to deposition of the Ti/Pt/Au contact.

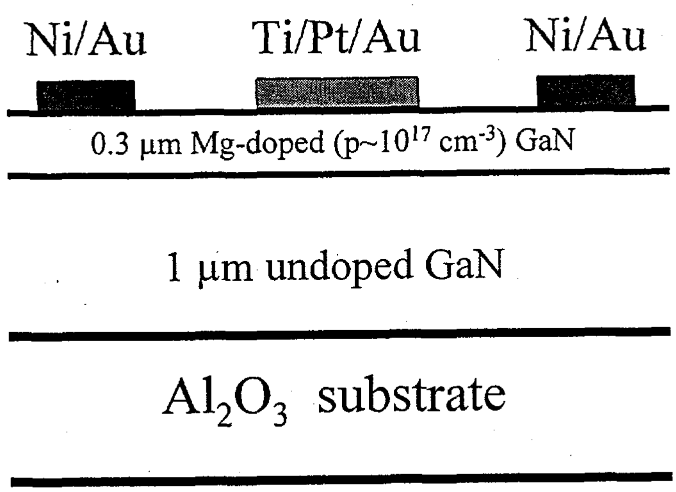
Figure 6. Variation of diode breakdown voltage in samples exposed to H_2 or Ar ICP discharges (500 W source power) at different rf chuck powers prior to deposition of the Ti/Pt/Au contact. The dc chuck self-bias during plasma exposure is also shown.

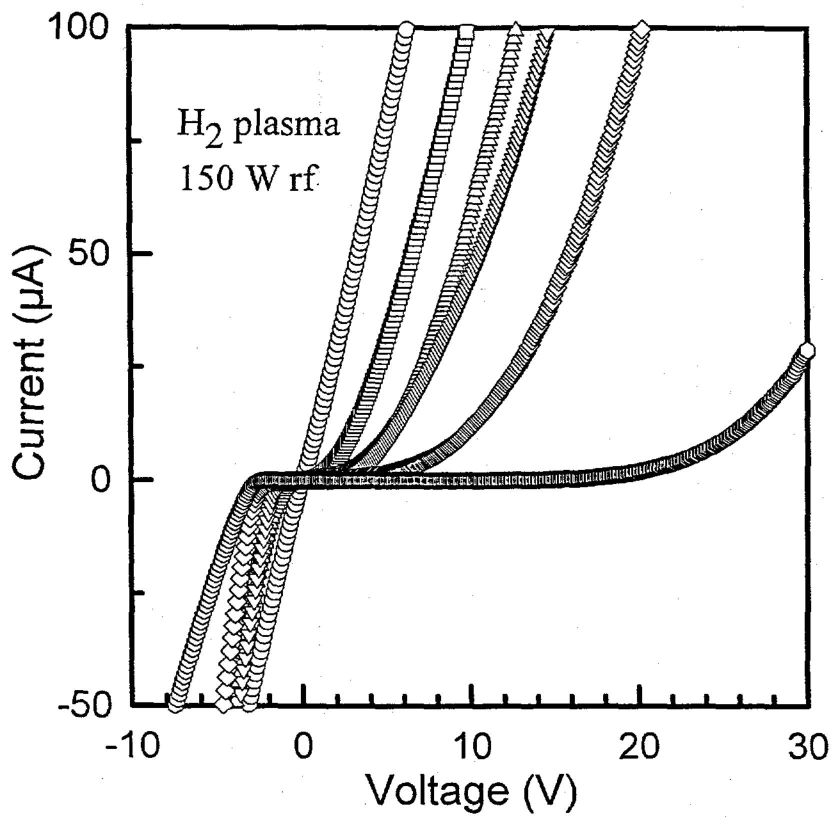
Figure 7. Wet etching rate of p-GaN in boiling NaOH solutions as a function of solution molarity.

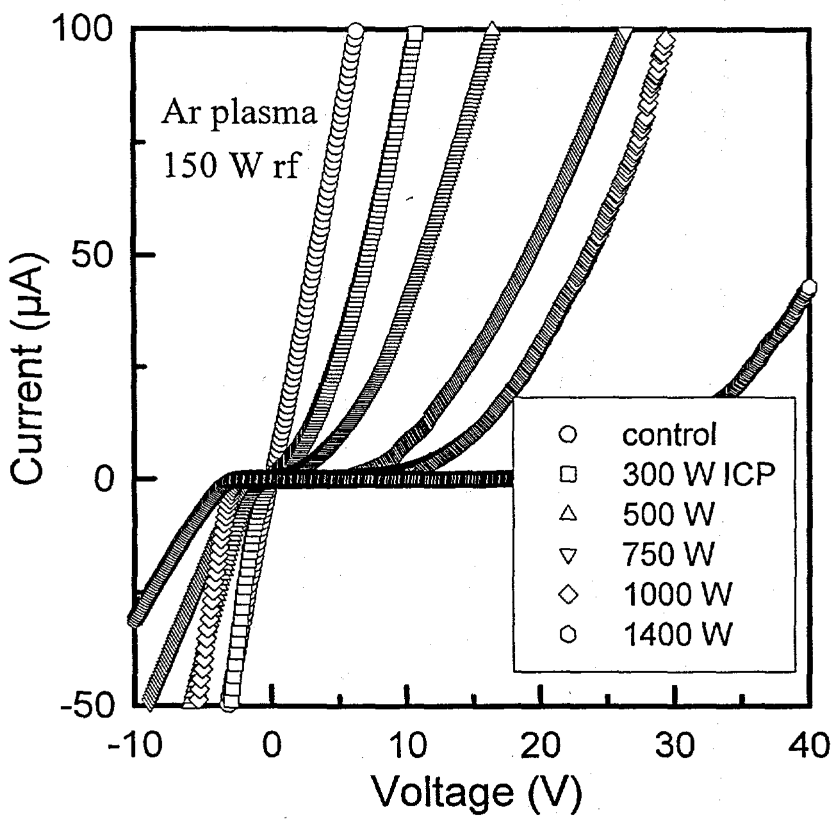
Figure 8. Wet etching rate of Ar plasma exposed (750 W source power, 150 W rf chuck power) GaN as a function of depth into the sample.

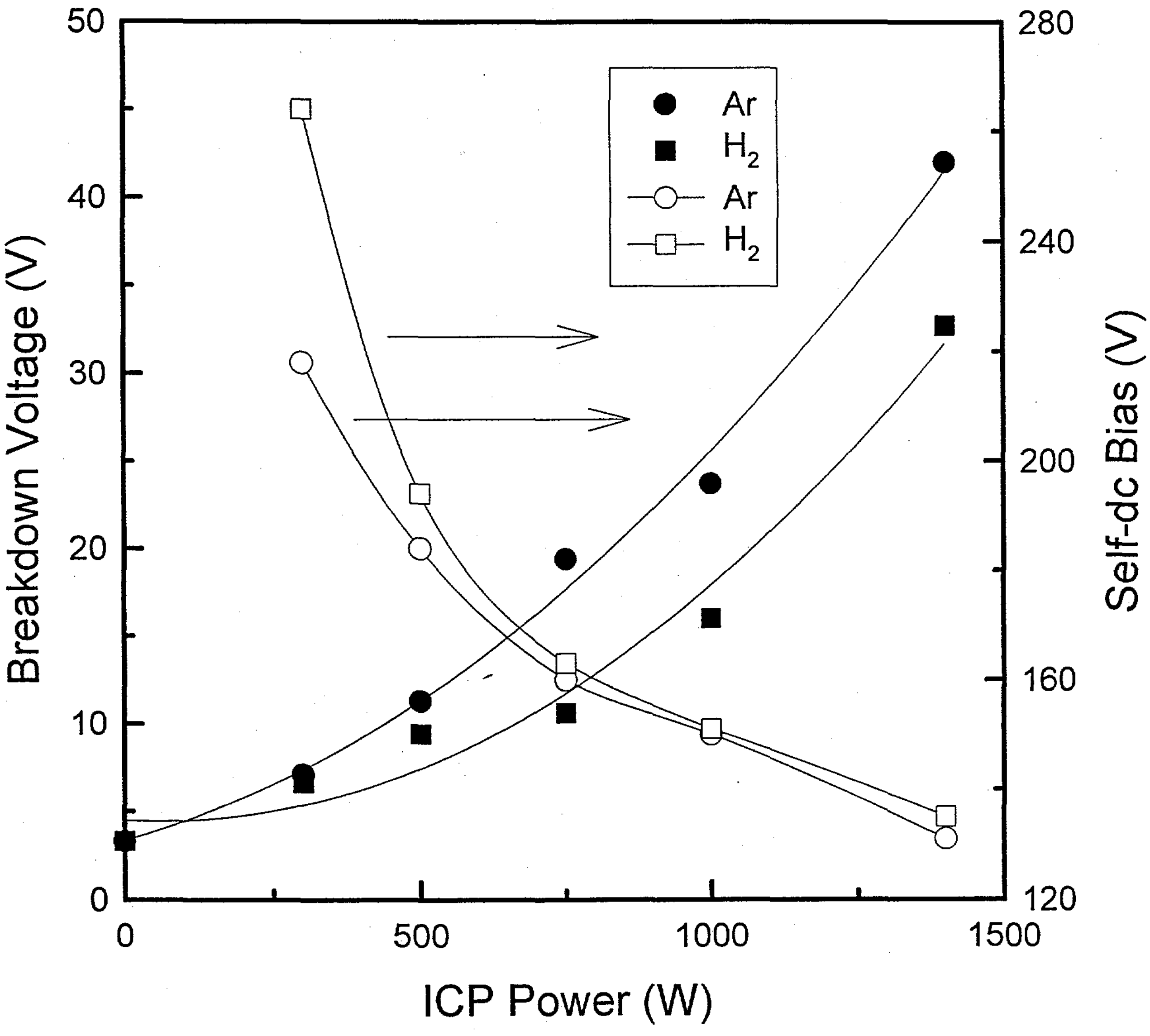
Figure 9. I-V characteristics from samples exposed to ICP Ar discharges (750 W source power, 150 W rf chuck power) and subsequently wet etched to different depths prior to deposition of the Ti/Pt/Au contact (top) and breakdown voltage as a function of depth removed (bottom).

Figure 10. I-V characteristics from samples exposed to ICP Ar discharges (750 W source power, 150 W rf chuck power) and subsequently annealed at different temperatures prior to deposition of the Ti/Pt/Au contact (top) and breakdown voltage as a function of annealing temperature (bottom).

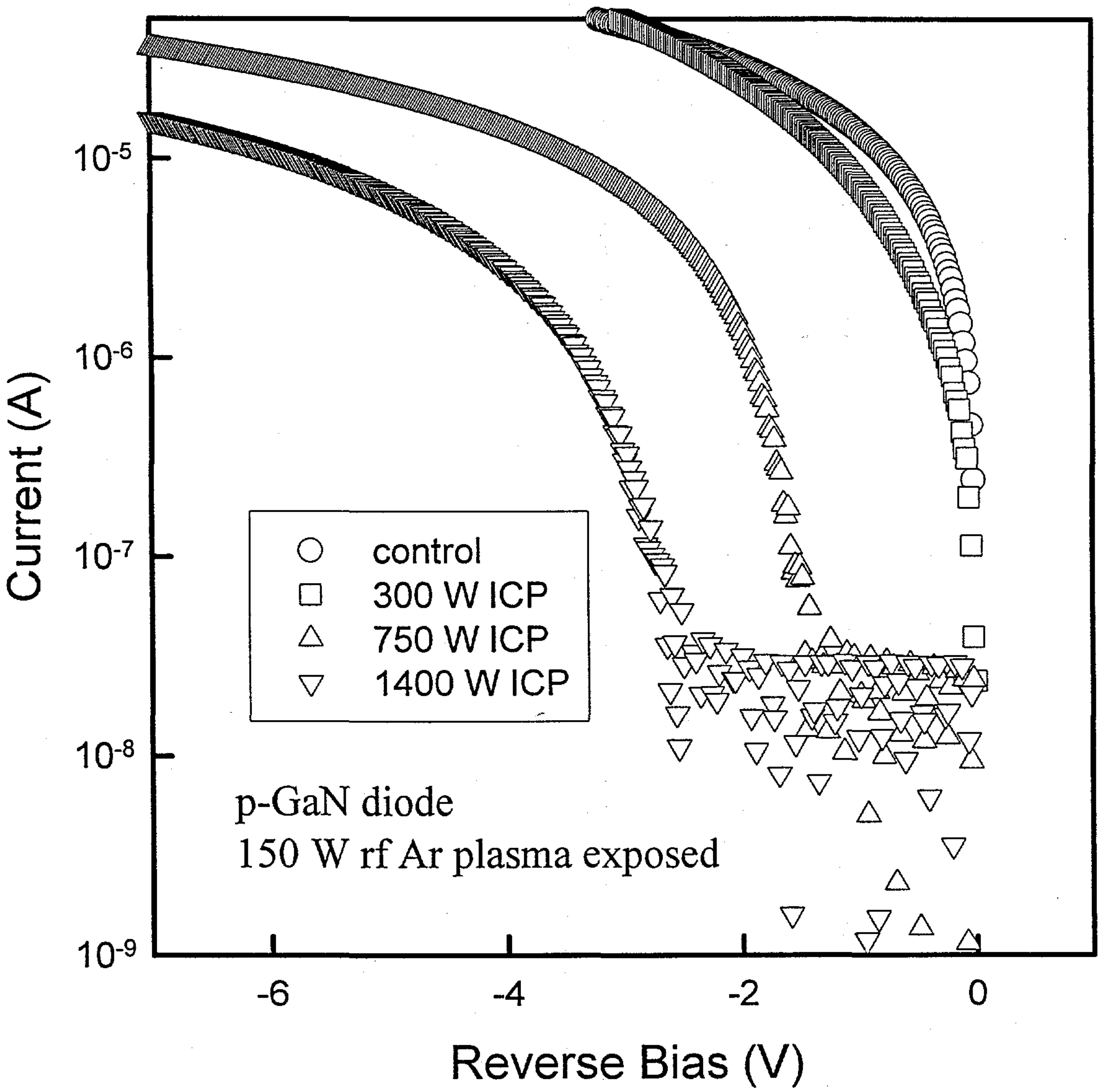

Ni/Au
Ti/Pt/Au
Ni/Au
0.3 μm Mg-doped (p~10^17 cm^-3) GaN
1 μm undoped GaN
Al2O3 substrate


H2 plasma
150 W rf
Current (μA)
Voltage (V)
100
50
0
-50
-10
0
10
20
30

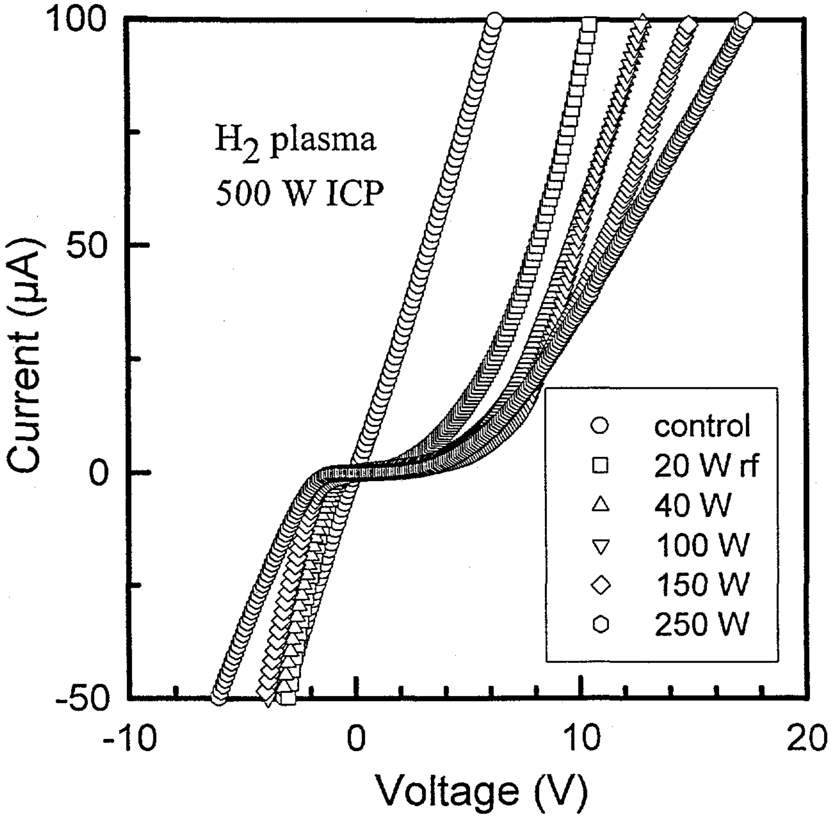

Ar plasma
150 W rf
Current (μA)
Voltage (V)
control
300 W ICP
500 W
750 W
1000 W
1400 W
100
50
0
-50
-10
0
10
20
30
40



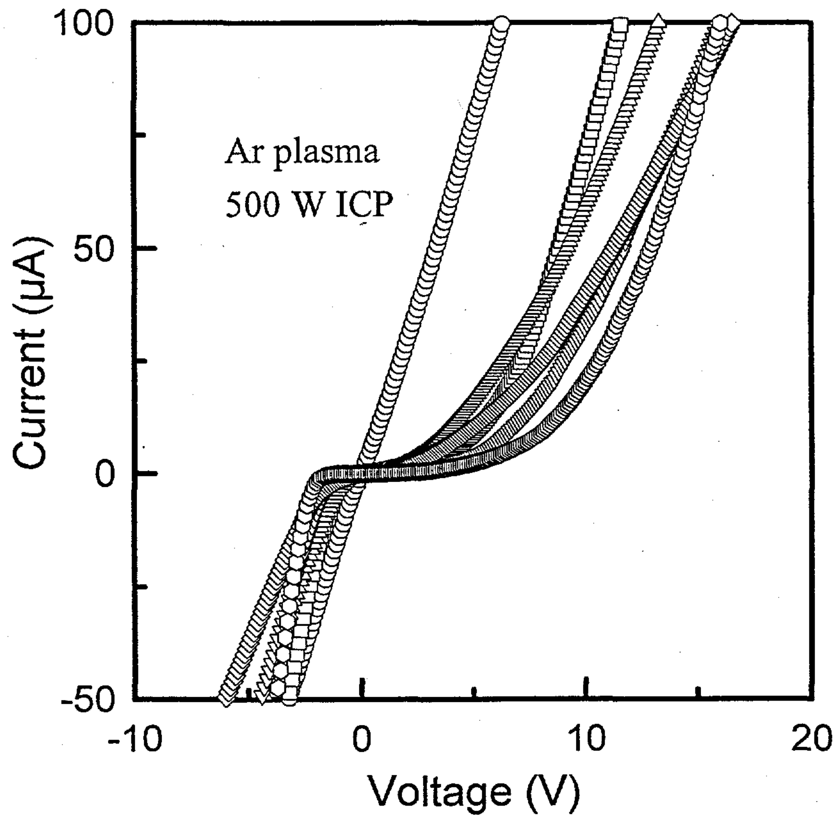
Breakdown Voltage (V)
Self-dc Bias (V)
ICP Power (W)
Ar
H_2
Ar
H_2
0
10
20
30
40
50
120
160
200
240
280
0
500
1000
1500



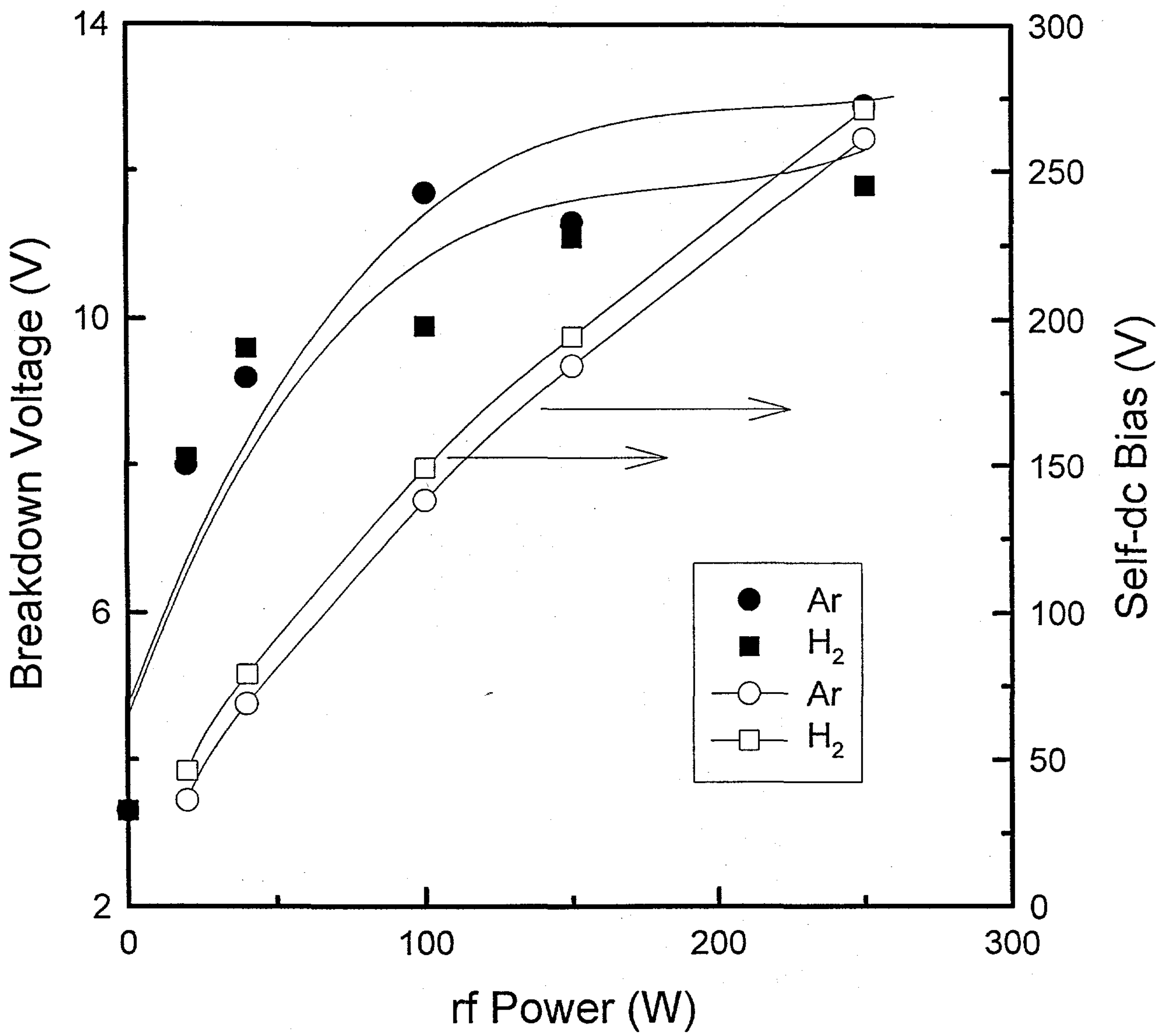
Current (A)
Reverse Bias (V)
10-5
10-6
10-7
10-8
10-9
-6
-4
-2
0
control
300 W ICP
750 W ICP
1400 W ICP
p-GaN diode
150 W rf Ar plasma exposed



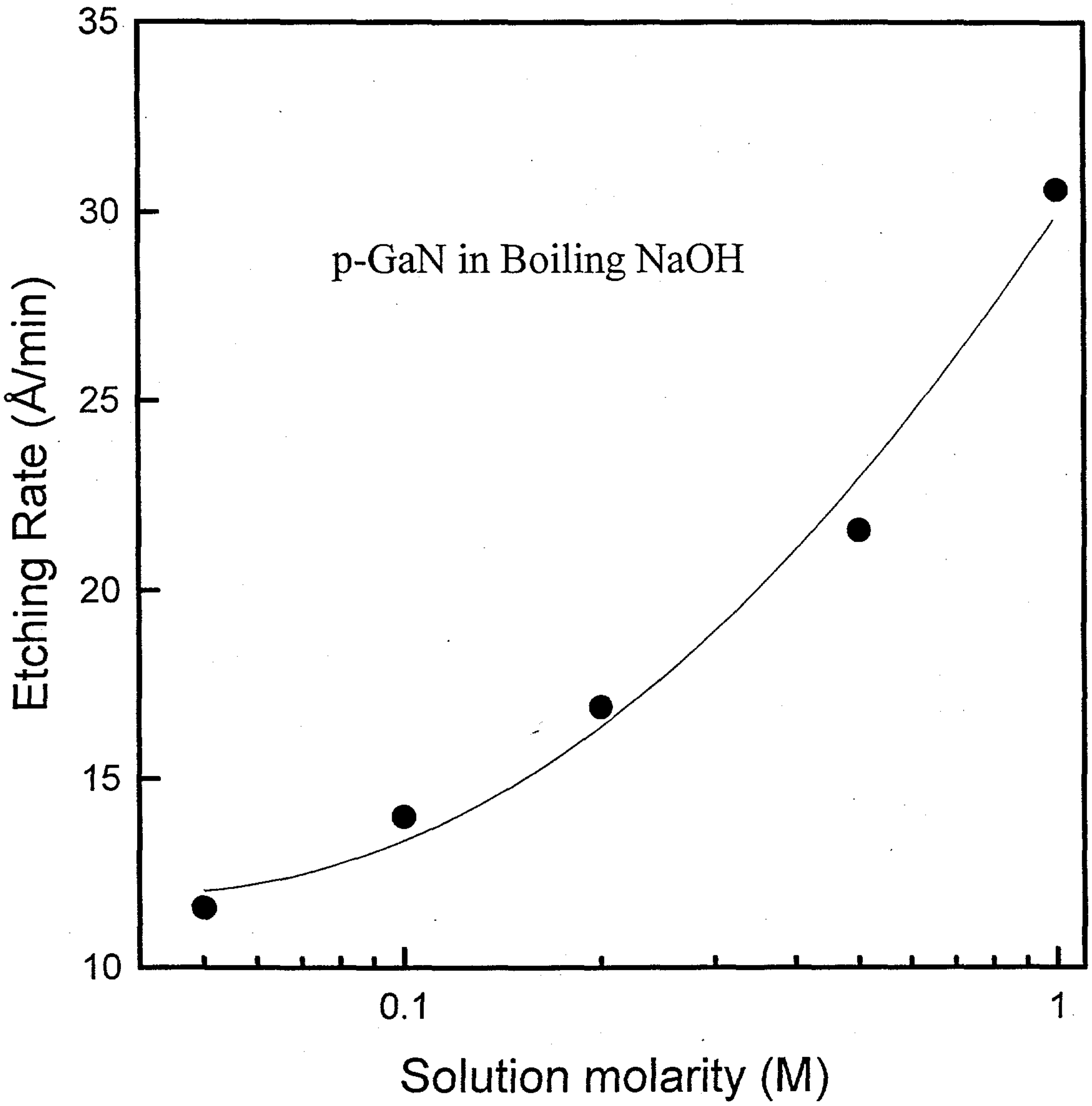
H$_2$ plasma
500 W ICP
Current (μA)
Voltage (V)
100
50
0
-50
-10
0
10
20
control
20 W rf
40 W
100 W
150 W
250 W



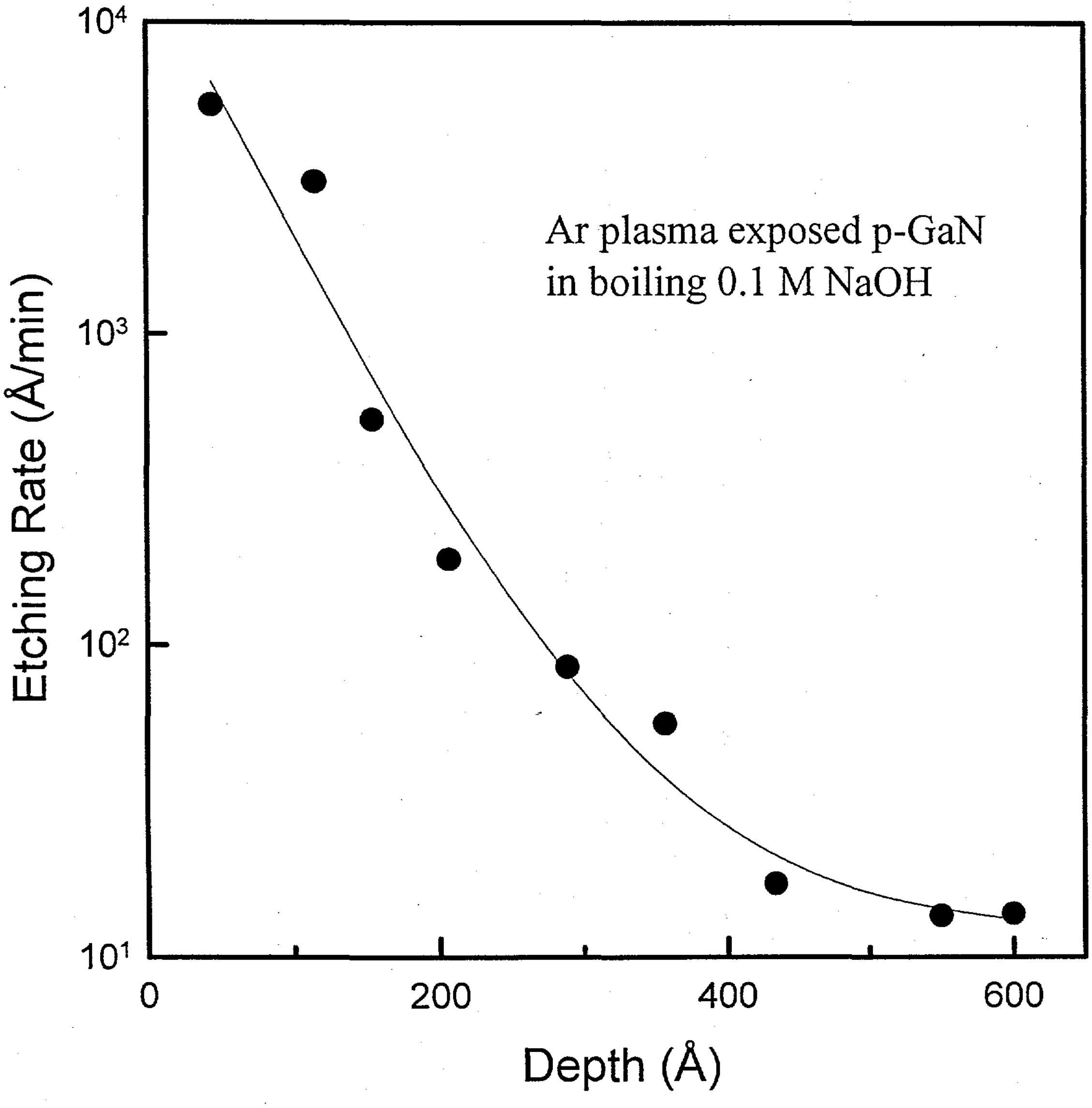
Ar plasma
500 W ICP
Current (μA)
Voltage (V)
100
50
0
-50
-10
0
10
20



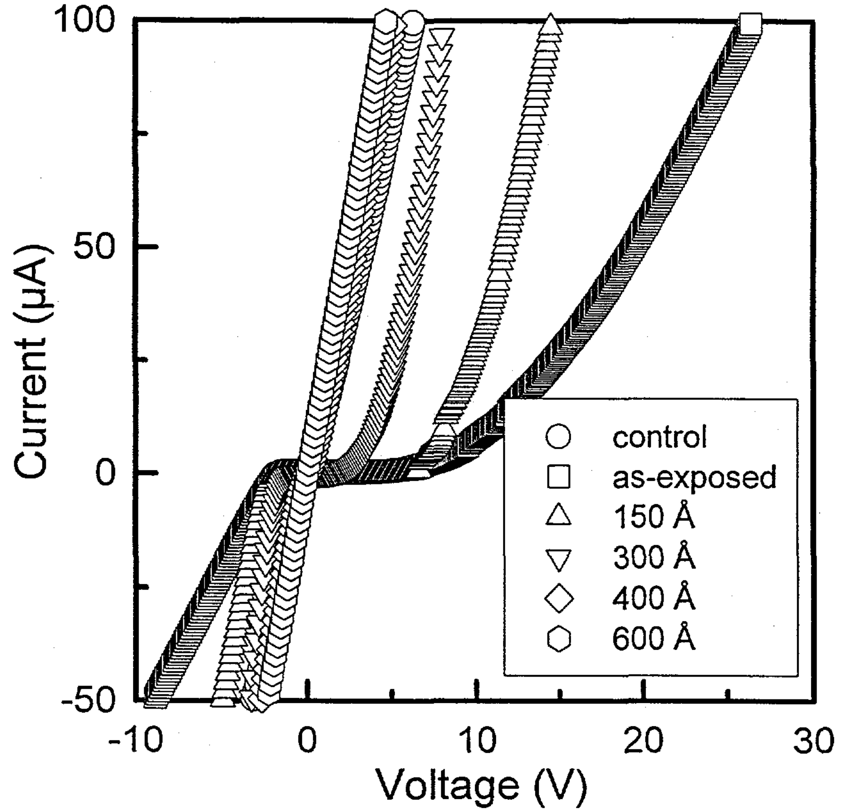
14
10
6
2
300
250
200
150
100
50
0
0
100
200
300
Breakdown Voltage (V)
Self-dc Bias (V)
rf Power (W)
Ar
H2
Ar
H2

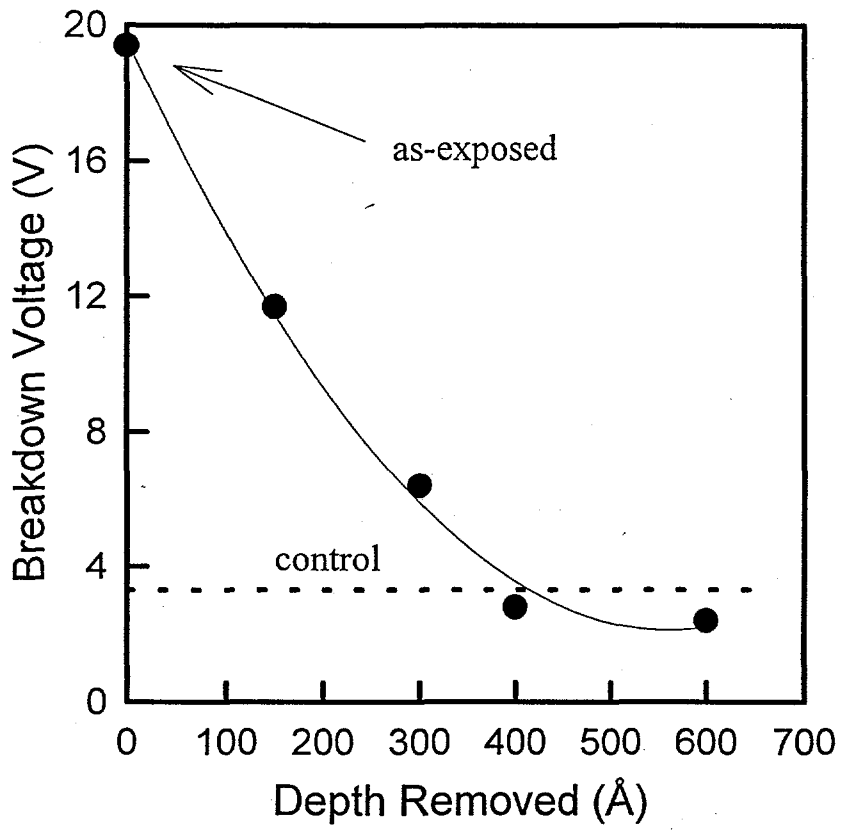


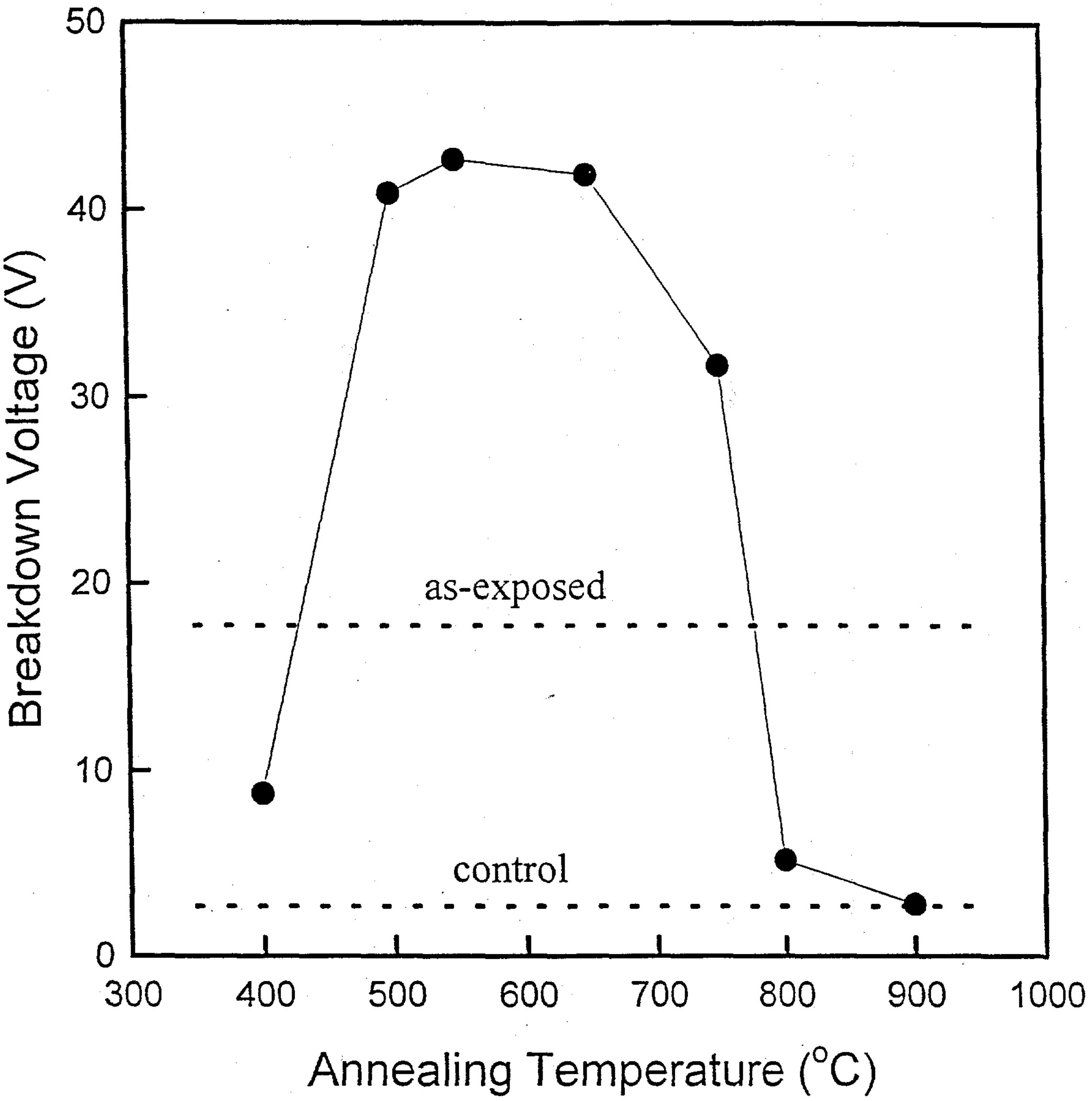
35
30
25
20
15
10
Etching Rate (Å/min)
p-GaN in Boiling NaOH
0.1
1
Solution molarity (M)



Etching Rate (Å/min)
10⁴
10³
10²
10¹
0
200
400
600
Depth (Å)
Ar plasma exposed p-GaN
in boiling 0.1 M NaOH


100
50
0
-50
-10
0
10
20
30
Current (μA)
Voltage (V)
control
as-exposed
150 Å
300 Å
400 Å
600 Å


20
16
12
8
4
0
0
100
200
300
400
500
600
700
Breakdown Voltage (V)
Depth Removed (Å)
as-exposed
control


50
40
30
20
10
0
Breakdown Voltage (V)
as-exposed
control
300
400
500
600
700
800
900
1000
Annealing Temperature (°C)