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# $Cl_2$/Ar High Density Plasma Damage in GaN Schottky Diodes

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## ABSTRACT

Inductively Coupled Plasma etching of GaN Schottky diodes in $Cl_2$/Ar discharges produces reductions in both reverse breakdown voltage and Schottky barrier height. The extent of these reductions is a function of both ion energy and ion flux. Two different post-etch treatments were performed in an attempt to remove the ion-damaged GaN surface layer, namely annealing in $N_2$ or UV-ozone oxidation followed by dissolution of the oxide. Both treatments provide only partial restoration of the diode properties.

## INTRODUCTION

GaN–based electronics offer the potential of high frequency operation at elevated temperatures (500 °C) and higher power levels than conventional GaAs or Si devices [1-9]. Significant progress has already been made in development of high performance GaN/AlGaN heterostructure field effect transistors [2-9] grown on $Al_2O_3$ or SiC substrates. Other prototype devices include a depletion-mode GaN MOSFET [10], GaN /AlGaN heterojunction 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 $N_2$ [17-19]. The Ga etch product in $Cl_2$-based discharges is $GaCl_3$, and this is less volatile than $N_2$ both from a pure chemical vapor presence and from a preferential sputtering viewpoint.

There has been relatively little work on understanding the effects of plasma processes on the electrical characteristics of GaN. 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 $N_2$ from the GaN surface does improve the specific contact resistance of n-type ohmic contacts because of the creation

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of a degenerately doped surface layer [23]. We have found previously that exposure of GaN to $H_2$ or $N_2$ Inductively Coupled Plasmas (ICP) prior to deposition of Schottky contacts creates a damaged region ~500Å deep that can be essentially restored to its original characteristics by annealing at 750 °C [24]. There are also situations where GaN device structures will employ a metal contact as a self-aligned etch mask. In this case it is of interest to examine the effects of plasma exposure on samples with existing Schottky contacts.

In this paper we report the results of a study of the effects of $Cl_2$/Ar ICP exposure on GaN Schottky devices. The degradation of reverse breakdown voltage ($V_B$) and Schottky barrier height ($\phi_B$) was strongly dependent on the incident ion energy and flux. Both annealing and UV ozone treatment were employed to try to remove the plasma damage.

## EXPERIENTAL

Diodes were fabricated on normally undoped (n~$10^{17}$cm$^{-3}$) GaN layers ~3μm thick grown on an $n^+$($10^{18}$cm$^{-3}$) GaN buffer on c-plane $Al_2O_3$ substrate [25]. Ohmic contacts were formed with lift-off Ti/Au subsequently annealed at 600 °C, followed by evaporation of the 250 μm diameter Pt/Au Schottky contacts through a stencil mask.

The samples were briefly exposed (~10secs) to 10 $Cl_2$/5Ar (total gas load 15 standard cubic centimeters per minute) ICP discharges in a Plasma Therm 790 reactor. 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 hold constant at 2 m Torr.

The current-voltage (I-V) characteristics of the diodes were recorded on a HP 4145A parameter analyzer. Barrier height ($\phi_B$) and ideality factor (n) were obtained from the forward I-V characteristic according to the relationship [26]:

$$J = A^{**}T^2 \exp(\frac{e\phi_B}{kT})[\exp(\frac{eV}{nkT} - 1)]$$

Where J is the current density, A** the effective Richardson constant, T the measurement temperature (25 °C), e the electronic charge and k is Boltzmann's constant. The reverse breakdown voltage ($V_B$) was defined as the voltage at which the current density was $3.06 \times 10^4$ mA/cm$^2$.

Some diodes were annealed at temperatures up to 800 °C after plasma exposure, while others were treated in UV-ozone at 25 °C for period up to 20 minutes, followed by rinsing in HCl solutions. Auger Electron Spectroscopy (AES) was performed in some cases.

## RESULTS ADN DISCUSSION

Figure 1 shows some typical I-V characteristics from GaN diodes after exposure to the ICP $Cl_2$/Ar discharges at fixed ICP source power and varying rf power. The latter parameter controls the average energy of ions (predominantly $Ar^+$ and $Cl_2^+$ in this case) incident on the samples. There is a clear degradation in $V_B$ as this rf chuck power is increased.

The dependence of $V_B$ and $\phi_B$ on rf chuck power is shown in the upper part of Figure 2. Both of these parameters decrease with increasing power. 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, 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. 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 $V_B$. In the case of semiconductors such as 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 [27, 28].

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.

As mentioned previously, past measurements on ICP damaged GaN surfaces have established the damage depth as being of order 500 Å [24]. One method for trying to remove damaged material is by oxidizing it by UV/ozone ($O_3$) exposure, followed by stripping of the oxide. Figure 4 shows the dependence of $V_B$ and $\phi_B$ on UV ozone treatment time. In each case after the oxidation, a 1:20, HCl: $H_2O$ solution was used for removal of the oxidized material. While there is some improvement in both parameters up to 5 min, there is no further improvement for longer times. We assume the oxidation distance is diffusion-controlled (i.e. dependent on $\sqrt{t}$), and from preliminary measurements we believe that only ~30 Å of GaN is oxidized and removed for 5 minute UV ozone exposure. Therefore the process would have to be repeated approximately 15-20 times to remove the damaged region of the GaN, assuming the oxidation rate remains the same deeper into the material. Use of a stronger HCl solution improves the $V_B$ value compared to use of the 1:20 solution (Figure 5), but there is no improvement in $\phi_B$.

Figure 6 shows the effect of anneal temperature on the recovery of $V_B$ and $\phi_B$. There is a clear improvement in $V_B$ for anneals in the range 500 - 700 °C, and little change thereafter and it remains lower than the unetched control value. However, $\phi_B$ changes very little with annealing. These results are somewhat different than in the case where the surface is exposed to the ICP discharge, annealed and then the Schottky contact is deposited(24). For that sequence, essentially full recovery of the electrical characteristics was obtained for 750 °C annealing. In the present case where the contact is in place we believe the metal begins to react with the GaN at ~600 °C, accounting for the lack of recovery of $\phi_B$ at higher temperatures.

The effect of annealing time at fixed temperature (700 °C) on $V_B$ and $\phi_B$ is shown in Figure 7. The improvement in both parameters leads to saturation beyond 60 secs. It would be expected that the recovery mechanism should be most critically dependent on temperature since most defect annealing processes involve dissociation and diffusion of defects and their complexes. In this case, the recovery would be dependent on the square root of annealing time and exponentially on temperature.

To establish the chemical state of the GaN surface at different stages, AES was performed. Figure 8 shows surface scans before (top) and after (lower) exposure to a 500 W source power, 50 W chuck power $Cl_2$/Ar discharge. 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 °C in $N_2$ restored some of this deficiency (Figure 8, bottom).

## SUMMARY AND CONCLUSIONS

The main points of our study may be summarized as follows:

1. ICP $Cl_2$/Ar discharges degrade the performance of GaN Schottky diodes, with ion energy and ion flux both playing important roles.
2. The degradation mechanism appears to be creation of a conducting, non-stoichiometric ($N_2$-deficient) near-surface region on the GaN.
3. 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.
4. Annealing at 700 - 750 °C also restores some of the initial reverse breakdown voltage characteristics, but little change in $\phi_B$ for Pt/Au contacts on GaN.

## ACKNOWLEDGEMENTS

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**Figure Captions**

Figure 1. I-V characteristics from GaN diodes after $Cl_2$/Ar plasma exposure (300W source power, 2m Torr) with different rf chuck powers

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 $Cl_2$/Ar plasma exposed GaN diodes (top) and of dc chuck self-bias and GaN etch rate under the same conditions (bottom)

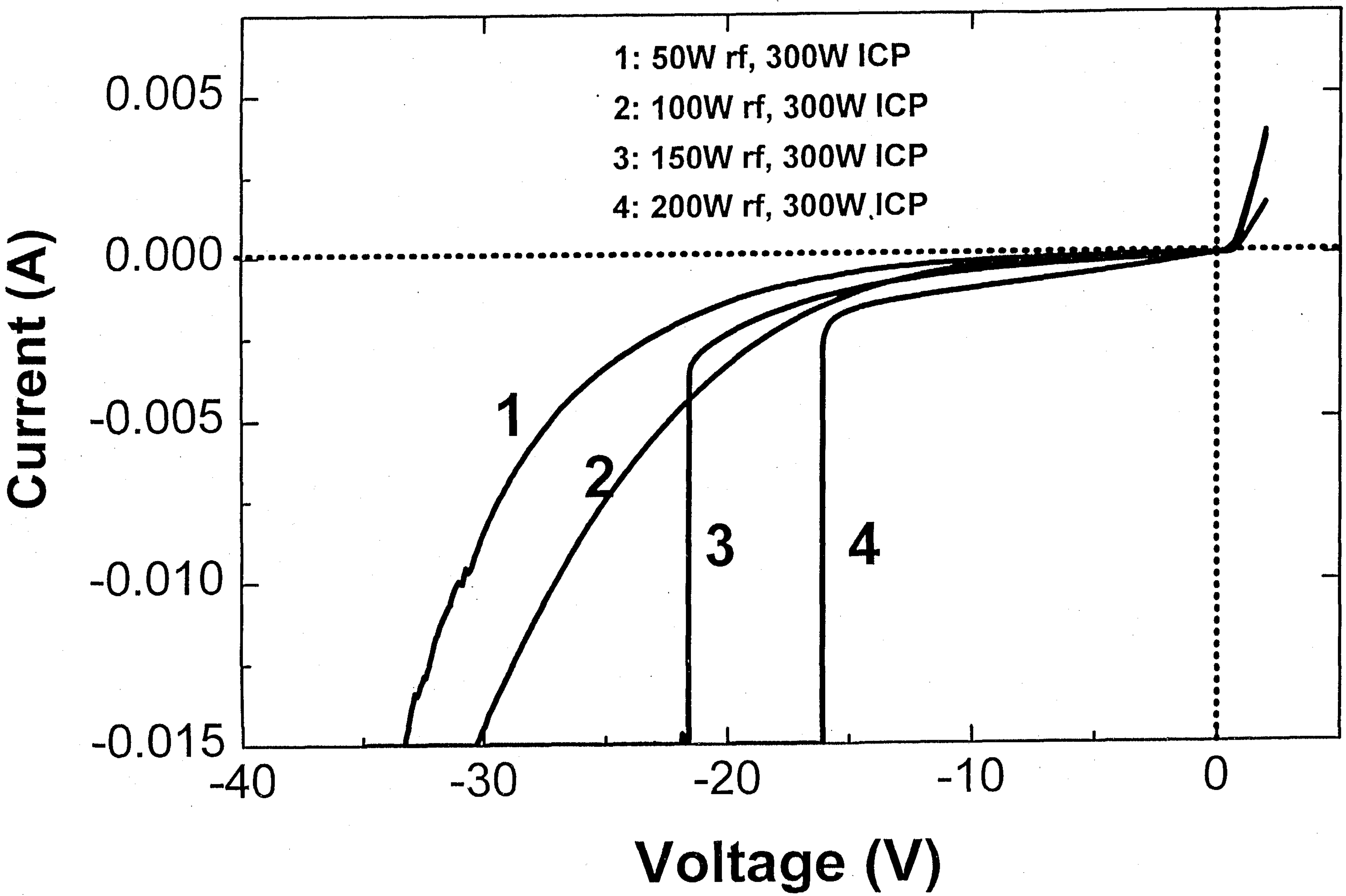
Figure 4. UV ozone oxidation time dependence of $V_B$ (top) and $\phi_B$ (bottom) in $Cl_2$/Ar plasma exposed GaN diodes. After oxidation, the samples were rinsed in 1HCl: $20H_2O$ for 1 min.

Figure 5. Dependence of $V_B$ (top) and $\phi_B$ (bottom) on process condition in $Cl_2$/Ar plasma exposed GaN diodes. After UV ozone oxidation, the samples were rinsed in 1HCl: $20H_2O$ for 1 min or aqueous HCl (35-38%) for 30-60 seconds.

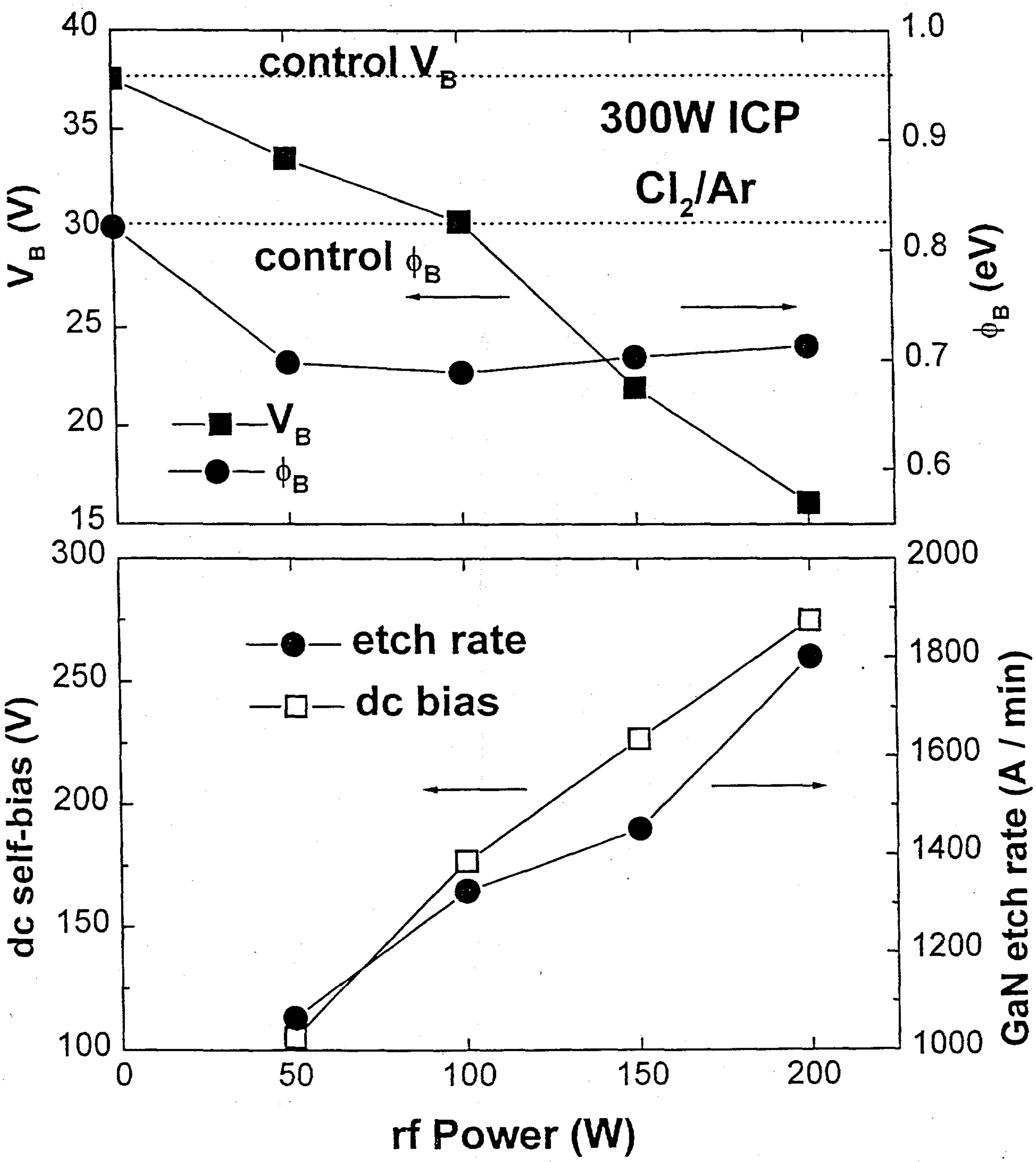
Figure 6. Annealing temperature dependence of $V_B$ (top) and $\phi_B$ (bottom) in $Cl_2$/Ar plasma exposed GaN diodes. Anneal time was 30 sec at each temperature.

Figure 7. Annealing time dependence (at 700 °C) of $V_B$ (top) and $\phi_B$ (bottom) in $Cl_2$/Ar plasma exposed GaN diodes.

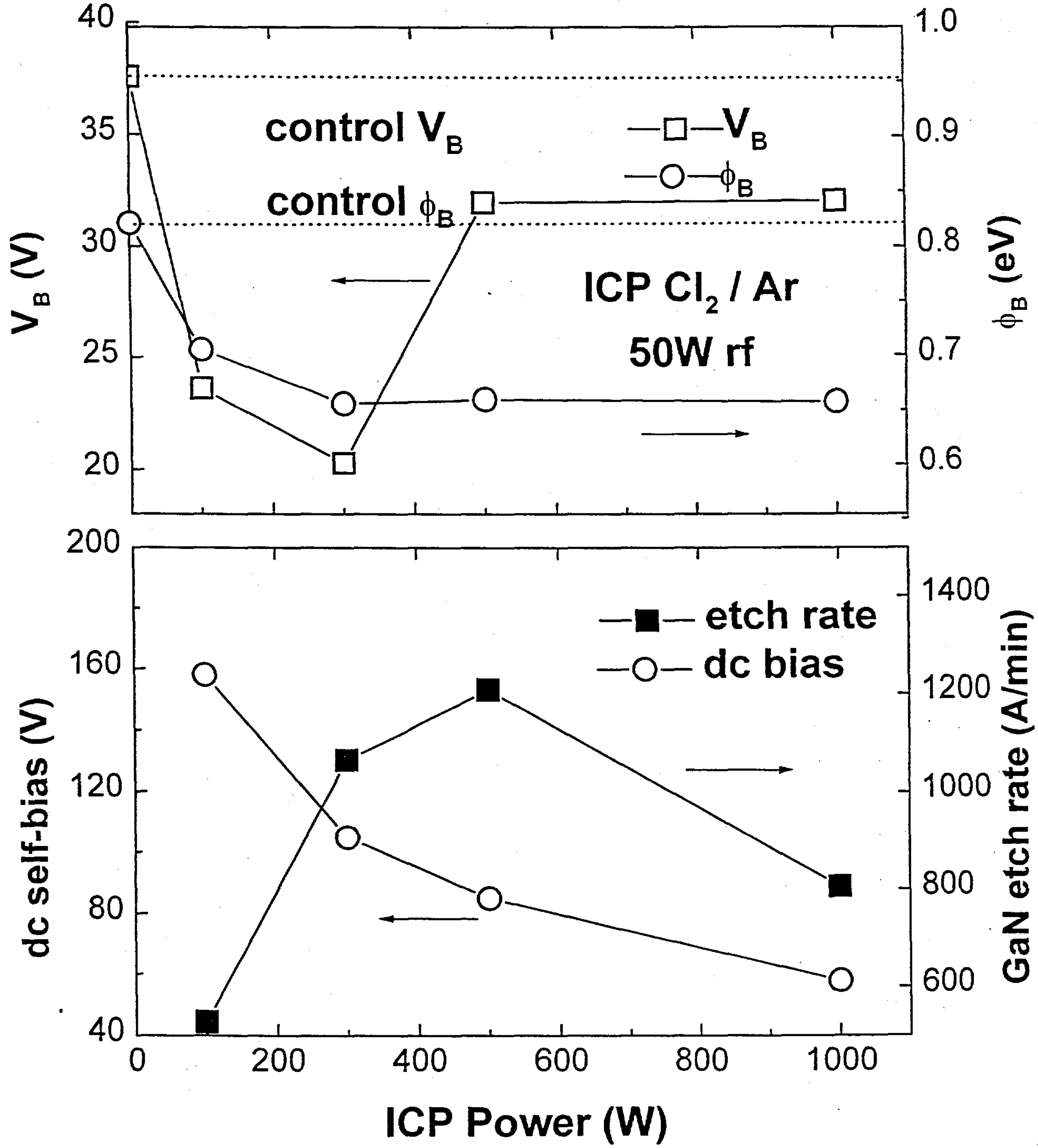
Figure 8. AES surface scans from GaN (top) or after (center) $Cl_2$/Ar plasma exposure, and subsequent annealing at 700 °C for 60 seconds (bottom).



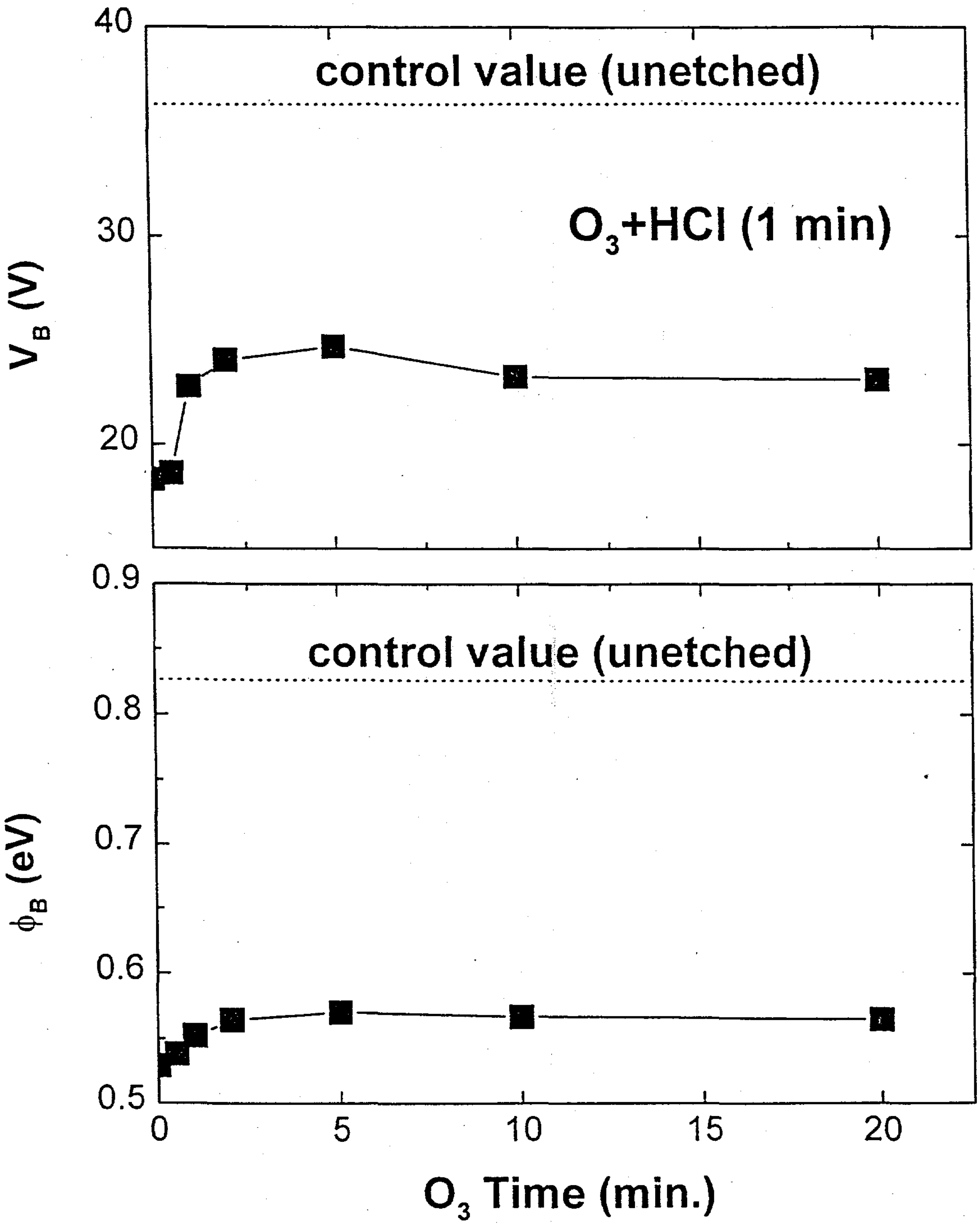
1: 50W rf, 300W ICP
2: 100W rf, 300W ICP
3: 150W rf, 300W ICP
4: 200W rf, 300W ICP
1
2
3
4
0.005
0.000
-0.005
-0.010
-0.015
Current (A)
-40
-30
-20
-10
0
Voltage (V)



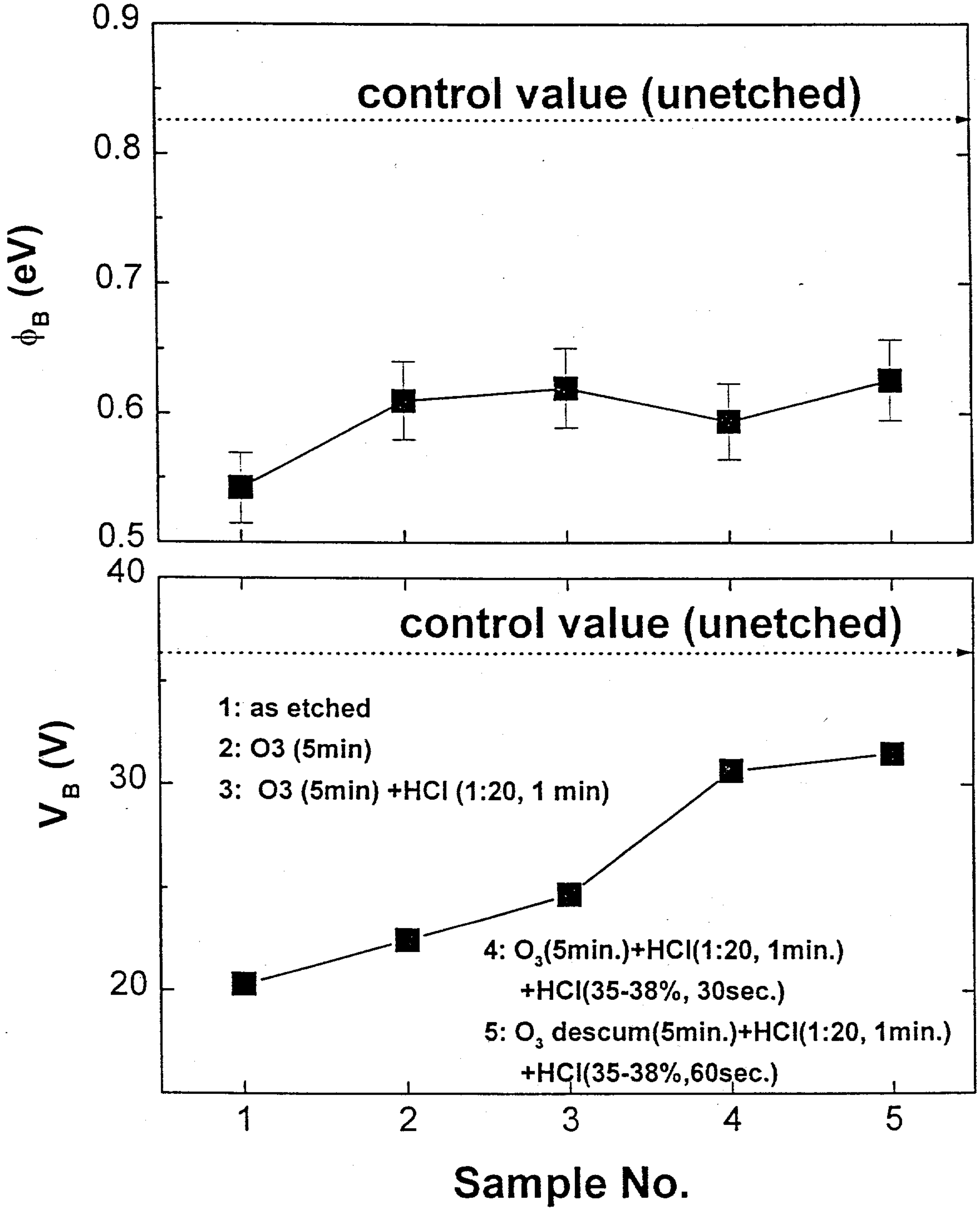
control $V_B$
300W ICP
$Cl_2/Ar$
control $\phi_B$
$V_B$
$\phi_B$
$V_B$ (V)
$\phi_B$ (eV)
40
35
30
25
20
15
1.0
0.9
0.8
0.7
0.6
etch rate
dc bias
dc self-bias (V)
GaN etch rate (A / min)
300
250
200
150
100
2000
1800
1600
1400
1200
1000
0
50
100
150
200
rf Power (W)

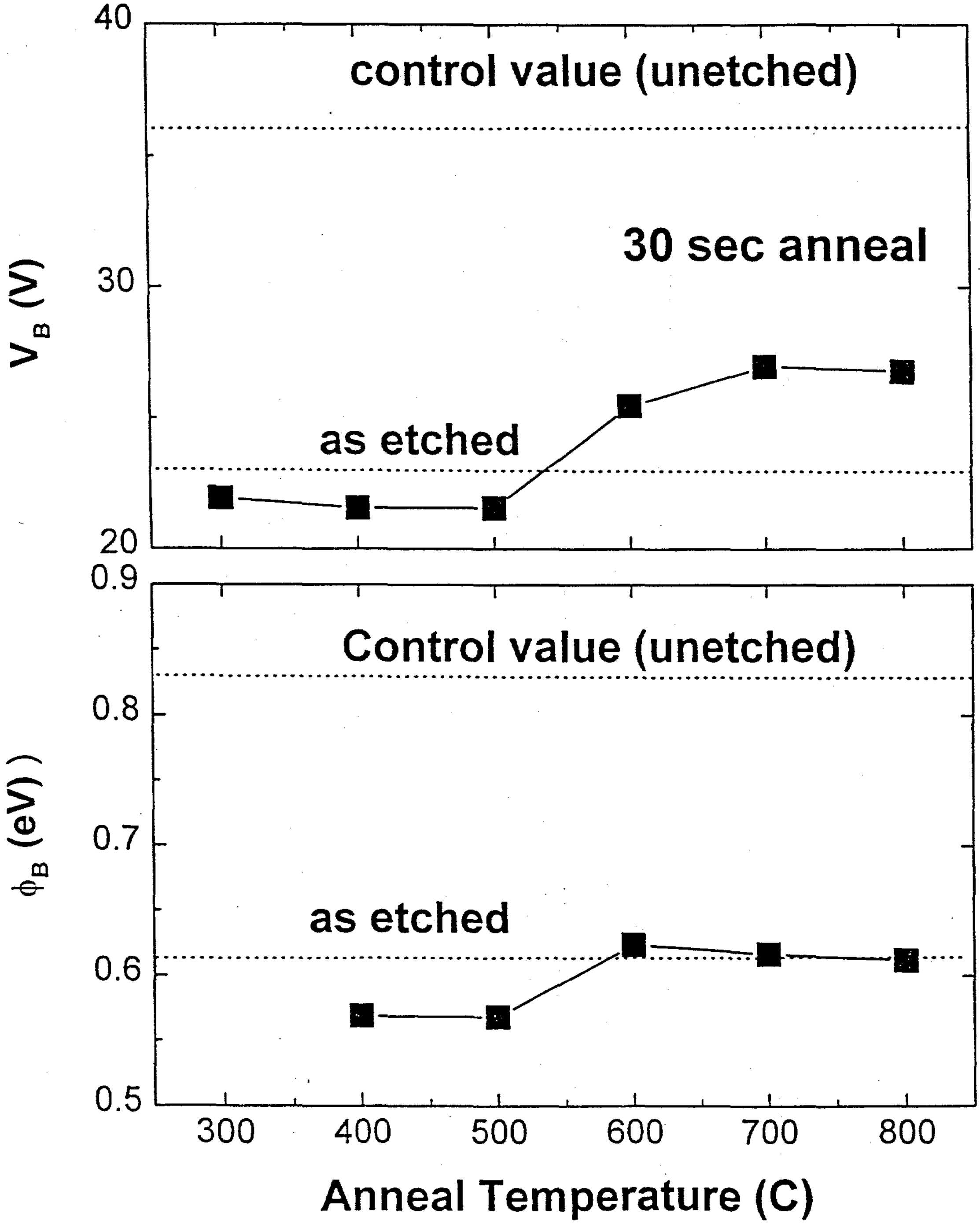


40
35
30
25
20
1.0
0.9
0.8
0.7
0.6
control $V_B$
control $\phi_B$
$V_B$
$\phi_B$
ICP $Cl_2$ / Ar
50W rf
$V_B$ (V)
$\phi_B$ (eV)
200
160
120
80
40
1400
1200
1000
800
600
etch rate
dc bias
dc self-bias (V)
GaN etch rate (A/min)
0
200
400
600
800
1000
ICP Power (W)

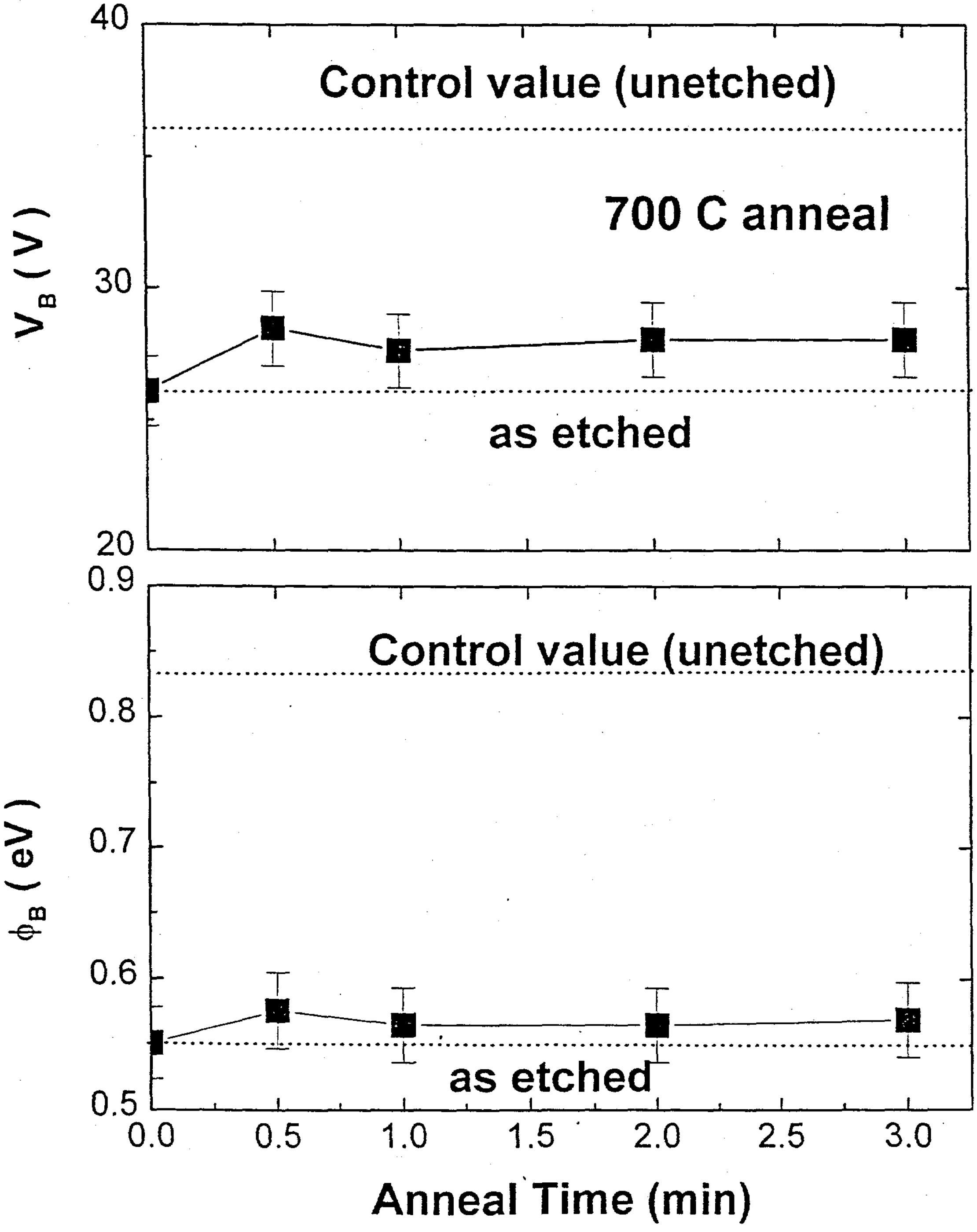


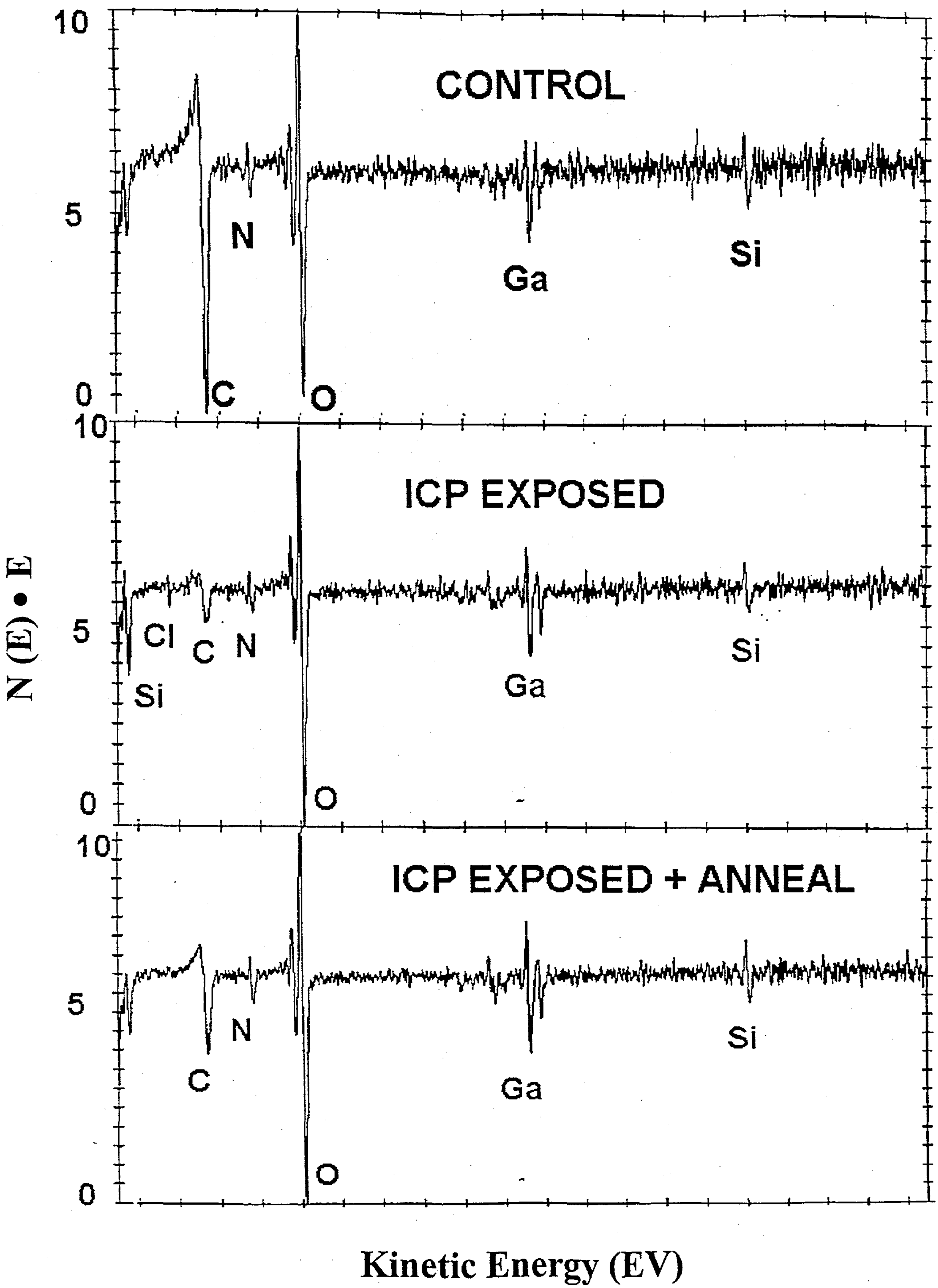
40
control value (unetched)
30
O3+HCl (1 min)
VB (V)
20
0.9
control value (unetched)
0.8
0.7
φB (eV)
0.6
0.5
0
5
10
15
20
O3 Time (min.)


control value (unetched)
0.9
0.8
0.7
0.6
0.5
$\phi_B$ (eV)
40
control value (unetched)
1: as etched
2: O3 (5min)
3: O3 (5min) +HCl (1:20, 1 min)
4: $O_3$(5min.)+HCl(1:20, 1min.) +HCl(35-38%, 30sec.)
5: $O_3$ descum(5min.)+HCl(1:20, 1min.) +HCl(35-38%,60sec.)
30
20
$V_B$ (V)
1
2
3
4
5
Sample No.



40
control value (unetched)
30 sec anneal
30
$V_B$ (V)
as etched
20
0.9
Control value (unetched)
0.8
$\phi_B$ (eV) )
0.7
as etched
0.6
0.5
300
400
500
600
700
800
Anneal Temperature (C)


Control value (unetched)
700 C anneal
as etched
$V_B$ (V)
40
30
20
Control value (unetched)
as etched
$\phi_B$ (eV)
0.9
0.8
0.7
0.6
0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Anneal Time (min)



CONTROL
ICP EXPOSED
ICP EXPOSED + ANNEAL
10
5
0
C
N
O
Ga
Si
Cl
N (E) • E
Kinetic Energy (EV)