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Plasma-Induced-Damage of GaAs during Etching of Refractory Metal Contacts

R. J. Shul, M. L. Lovejoy, A. G. Baca, J. C. Zolper, D. J. Rieger, M. J. Hafich, and R. F. Corless

Sandia National Laboratories, Albuquerque, NM 87185

C. R. Vartuli

University of Florida, Gainesville, FL

The effect of plasma-induced-damage on the majority carrier transport properties of GaAs has been studied by monitoring changes in sheet resistance (R_S) of thin conducting layers under various plasma conditions including etch conditions for refractory metal contacts. R_S determined from transmission line measurements are used to evaluate plasma-induced-damage for electron cyclotron resonance (ECR) and reactive ion etch (RIE) conditions by varying the thickness of doped epitaxial layers. We speculate that plasma-induced-damage in the near surface region plays a major role in explaining the damage mechanism observed in this study. Very consistent trends have been observed where R_S increases with increasing ECR and RIE dc-bias, increasing microwave power, and decreasing pressure, thus showing R_S increases as either the ion energy or ion flux increases. We have also observed that R_S is lower for samples exposed to the RIE than the ECR, possibly due to higher ion and electron densities generated in the ECR and higher pressures in the RIE. We have also observed R_S dependence on ECR plasma chemistry where, R_S is lower in SF_6/Ar plasmas than Ar and N_2 plasmas possibly related to interactions of F or S atoms with the GaAs surface. Moderate anneal temperatures (200 to 500 °C) have shown significant R_S recovery.

I. INTRODUCTION

Refractory metal thin films for non-alloyed ohmic and Schottky contacts are finding wide application in the fabrication of high-speed GaAs field-effect transistors (FETs) and heterojunction bipolar transistors (HBTs). Refractory metals can be used in a self-aligned gate process as the ion implantation mask for the formation of source and drain regions[1] for GaAs metal-semiconductor FETs (MESFETs). The plasma etch, which is often done using fluorine-containing plasmas,[2-7] must be anisotropic to accurately mask the implant area. Anisotropic profiles can be enhanced by increasing the dc-bias, however this also increases the potential for kinetic damage to the GaAs surface. Refractory metal features are typically etched with a 20% overetch period to account for non-uniformities in both the etch and deposition of the films. During this period, the GaAs surface is directly exposed to the plasma and can incur plasma-induced-damage. Although reactive ion etching (RIE) and electron cyclotron resonance (ECR) etches have been reported to yield refractory metal etching with sub-micron dimensions and anisotropic profiles, plasma-induced-damage to the GaAs active layers has not been reported.

The bombardment of GaAs or other III-V semiconductors with energetic ions generated during plasma etching can produce lattice damage for ions with an energy greater than the displacement energy of the host atoms as well as surface related damage. As these energetic ions strike the sample, damage as deep as 100 nm can occur,[8] causing degradation of electrical properties of the device. This damage can range from simple Frenkel pairs consisting of a vacancy and the displaced atom, implanted etch ions, or more complex defects such as divacancies, trivacancies, and clusters of vacancies or interstitials.[9] Surface related damage can include broken bonds, embedded ions, formation of dangling bonds, or deposition of material on the sample. Attempts to minimize the damage by reducing the ion energy below the damage threshold for compound semiconductors (< 40 eV)[10] or by increasing the chemical component of the etch results in a more isotropic etch and significantly limits minimum dimensions. Comparisons of ECR and RIE etching have shown less damage produced in the ECR due to the formation of high density plasmas at low pressures and low ion energies.[11-15] However, anisotropic profiles in the

ECR are achieved by superimposing an rf-bias (13.56 MHz) on the sample which increases the acceleration of energetic ions to the sample thereby increasing the potential for kinetic damage to the surface.

In this paper we report the effect of plasma-induced-damage on the majority carrier transport properties of GaAs by monitoring changes in the sheet resistance of thin conducting layers under a variety of ECR and RIE plasma conditions simulating those used during refractory metal etching. Sheet resistances (R_S) determined from transmission line measurements (TLMs) are used to evaluate the plasma-induced-damage for ECR and RIE conditions by varying the thickness of doped epitaxial layers. These data are compared to baseline samples which have not been exposed to a plasma. ECR plasma chemistries including SF_6/Ar, Ar, and N_2 at dc-biases ranging from 0 to 250 V and microwave powers from 150 to 500 W and RIE SF_6/Ar plasmas at 25 to 300 W rf-power were studied.

II. EXPERIMENTAL

The GaAs samples used in this study were grown by conventional molecular beam epitaxy on a Varian Gen II system. All layers were grown at a substrate temperature of 590°C and a growth rate of 1 μm/hr. Beryllium was the p-type dopant. The epitaxial structures were grown on 2 inch, undoped, (100) GaAs substrates and consisted of a 0.8 μm undoped GaAs buffer layer, a doped conduction layer of various thicknesses, and a heavily doped 100 Å ohmic contact p^+ layer. Four different thicknesses of p-type doped conduction layers were grown to maintain an approximate depletion layer thickness 1/3 of the total doped thickness (the depletion layer thickness for the lowest doped sample was 1/4 of the total doped thickness). The epitaxial layer thickness and doping were: 3200 Å, 1.5 E17 cm^{-3}; 1800 Å, 3E17 cm^{-3}; 1150 Å, 6E17 cm^{-3}; and 900 Å, 1E18 cm^{-3}. Growth was interrupted for 60 seconds before beginning the top layer to allow a change in the Be effusion cell temperature and insure an ohmic contact layer doped to 1 to 2E19 cm^{-3}.

BeAu ohmic contacts were used rather than refractory metals so the R_S could be measured before and after plasma exposure thus eliminating the need for a subtractive etch. Ohmic contacts for TLM patterns were formed by metal evaporation and liftoff using standard photolithography techniques. The contacts were deposited by thermal evaporation of Au and Be wires with total Be content of 2% by weight and were alloyed at 380 °C for 15 s. The heavily-doped semiconductor region at the surface was removed by a timed wet etch with a H_3PO_4:H_2O_2:H_2O (1:4:495) solution. The wet etch removed approximately 125 ± 25 Å of GaAs.

RIE plasmas were generated in a 13.56 MHz rf-powered parallel plate Plasma-Therm Batchtop RIE system. Gases were distributed through a showerhead arrangement located in the upper electrode. The lower electrode was 17.8 cm in diameter with an interelectrode spacing of approximately 10 cm and was completely covered with a 3.2 mm thick quartz plate. Samples were attached to the quartz plate with a low-vapor-pressure thermal paste to ensure good thermal conduction. RIE plasma conditions were: 50 °C electrode temperature, 12.5 sccm total gas flow, 8 mTorr total pressure, and dc-biases ranging from 130 to 550 V.

The ECR plasma reactor used in this study was a load-locked Plasma-Therm SLR 770 etch system with an ECR source operating at 2.45 GHz. Ion bombardment energies were provided by superimposing an rf-bias (13.56 MHz) on the sample. Samples were mounted on an anodized Al carrier that was clamped to the cathode and cooled with He gas. Gases were introduced through an annular ring into the chamber just below the quartz window. To minimize field divergence and optimize plasma uniformity and ion density across the chamber, an external secondary collimating magnet was located on the same plane as the sample and a series of external permanent rare-earth magnets were located between the microwave cavity and the sample. ECR etch parameters used in this study were: 10°C electrode temperature, 25 sccm of total gas flow (5 sccm SF_6 and 20 sccm Ar), 1 to 10 mTorr total pressure, 125 to 500 W of applied microwave power, and dc-biases ranging from 0 to 250 V.

Plasma-etch-induced damage effects were evaluated by calculating R_s with the standard transmission line-method analysis. Devices for the study had 50 x 100 μm^2 contacts approximately spaced 3, 5, 9, 13, and 20 µm apart. Four-point probe measurements were performed at typically 25 points in the current densities range of ±1000 A/cm^2 for each structure.

For the devices with finite resistance, excellent linearity (i.e., ohmic behavior) was observed. At least four devices were measured to verify that nominal characteristics were obtained. The contact spacing which was used in the analysis was measured by SEM imaging. Linear regression of measured resistance versus spacing yielded excellent fits with correlations of 1.000. The data reported is the average of the measured devices and the uncertainty is the standard deviation.

To evaluate the effect of high temperature on the R_S, samples were annealed in an Addax AET rapid thermal annealer in flowing argon preceded by a three cycle pump/purge sequence to reduce the background oxygen level. In the annealer, samples were contained in a SiC coated graphite crucible with thermocouples monitoring the temperature at two points on the crucible. Anneal times were 30 s at the prescribed set point ±10 °C.

III. RESULTS AND DISCUSSION

A. Effects on Electrical Properties

In this study GaAs samples were exposed to ECR and RIE plasmas for 1 minute. SF_6/Ar plasmas were used in both the ECR and RIE to simulate the plasma chemistry for refractory metal etching and Ar and N_2 ECR plasmas were used to determine the effect of plasma chemistry. Calculated R_S are displayed versus dc-bias, microwave power, and plasma chemistry in Figs. 1 to 4. R_S for samples exposed to the plasma are compared to baseline samples which have not been exposed to a plasma and have R_S values of 7.12 kΩ/square for 1.5E17 cm^{-3}, 6.57 kΩ/square for 3.0E17 cm^{-3}, 5.90 kΩ/square for 6.0E17 cm^{-3}, and 4.72 kΩ/square for 1.0E18 cm^{-3}. The amount of GaAs sputtered during exposure to the various plasma conditions has been evaluated using a SEM and have shown minimal material removal (0 to 150 Å) under most conditions. However, at 500 W ECR microwave power and 150 V dc-bias for SF_6/Ar and Ar plasmas we have observed GaAs loss of 600 ± 100 Å.

R_S is plotted as a function of dc-bias for samples exposed to RIE and ECR SF_6/Ar plasmas in Figs. 1 and 2, respectively. In all cases, R_S increases with increasing dc-bias due to higher ion energies. R_S obtained from samples exposed to the RIE are comparable to baseline samples for all 4 doping levels at dc-biases of 135 and 250 V. At 400 and 550 V RIE dc-bias, several samples show infinite R_S due to the increased ion energy. However, R_S for the 1.5E17 cm^{-3} doped sample is less than 30 kΩ/square despite the high dc-bias. In the ECR SF_6/Ar plasma, R_S increases with dc-bias at 125 (Fig. 2A) and 500 W microwave power (Fig. 2B). Similarly, for Ar plasmas at 125 and 250 W ECR microwave power and N_2 plasmas at 125 W ECR microwave power we observe an increase in R_S as the dc-bias is increased. Increasing the ion energy shows an increase in R_S for both the ECR and RIE independent of plasma chemistry and microwave power. Lower R_S is observed from samples exposed to the RIE plasma than those exposed to the ECR despite higher dc-biases in the RIE. This may be due to the difference in the ion density generated in the ECR which is approximately 4 orders of magnitude greater than that in the RIE as well as lower ECR pressures.

R_S shows a strong dependence on ECR microwave power as can be seen in Fig 3. As the ECR microwave energy is increased for an Ar plasma, R_S increases independent of dc-bias. With 0 rf-biasing (~ 10 V dc-bias), R_S increases to a maximum of 14.9 kΩ/square at 500 W microwave power which is a factor of 2.4 greater than the baseline value (Fig. 3A). At 50 V dc-bias, R_S shows the same trend with microwave power increasing to infinity for all samples with the exception of the 1.5E17 cm^{-3} doped sample which is 16.8 kΩ/square (Fig. 3B). A similar trend is observed for SF_6/Ar ECR plasmas where R_S at 500 W microwave power is much greater than R_S at 125 W microwave power at 50 and 150 V dc-bias (Fig. 2). This trend may be due to increased ion flux at higher microwave powers thereby increasing the plasma-induced-damage of the GaAs surface.

R_S is plotted as a function of plasma chemistry for the 4 different GaAs doped epitaxial layers in Fig. 4. As the dc-bias is increased, R_S increases regardless of the plasma chemistry for all epitaxial layers. The Ar and N_2 data are within a factor of 2. However, the SF_6/Ar R_S data is consistently lower than both the Ar and N_2 data which may be related to interactions of the F or S atoms with the GaAs surface.

Finally, R_s is evaluated as a function of pressure for a N_2 plasma at 125 W ECR microwave power and 50 V dc-bias. R_s decreases as the pressure is increased from 1 to 10 mTorr possibly due to lower ion energies and higher recombination of electrons and ions at higher pressures thereby reducing the ion flux. This is consistent with our observation that R_s is lower for samples exposed to the RIE at 8 mTorr than those exposed to the ECR at 1 mTorr.

B. Damage Mechanism

Samples with different dopings and active layer thicknesses were chosen so that the effective damage depth and alteration of surface potentials could be assessed. The higher doped samples contain a depletion-layer thickness that is approximately 1/3 of the total active layer thickness. For the 1.5E17 doped sample, the depletion layer thickness is approximately 1/4 of the total active layer thickness. An assumption of a "damaged-layer thickness" has successfully been used to model plasma damage to thin, highly-doped GaAs:Si at one doping level.[16] In this model the damaged layer thickness, W_a, is given by,

$$W_a = W_o(\Delta\sigma/\sigma) + (1 + \Delta\sigma/\sigma)(2\varepsilon\Phi_{ss}/qN_D)^{1/2} - (2\varepsilon E_a/qN_D)^{1/2}$$

where Wo is the total active layer thickness, σ is the conductance, $\Delta\sigma$ is the change in conductance upon exposure to the plasma, Φ_{ss} is the built-in potential, and E_a is the deep acceptor level. We modeled our data for the SF_6/Ar plasma chemistry in the RIE at 250 and 400 V dc-bias, as well as the Ar ECR data at 125 W microwave power and dc-biases of 0 and 50 V. Values of 0.7 and 0.55 were used for E_a and Φ_{ss}, although the results were not very sensitive to the choice of these numbers. These data are not fit well by a constant "damaged-layer thickness" as shown in Table 1. The calculated W_a varied from 50 to over 100 % as a function of the doping and were not sensitive to small variations (≈100 Å) in the active layer thicknesses due to uncertainties in the wet etch and possible sputter etching. We speculate that plasma-induced-damage in the near surface region plays a major role in explaining the damage mechanism observed in this study and experiments are underway to verify this. This observation is consistent with the large differences in R_s that we observed between the SF_6/Ar plasma chemistry and the Ar and N_2 plasmas in the ECR.

In Figures 1-3 , an ordering of the data with the general trend of lower R_S after plasma exposure for samples with lower doping is expected, however under certain plasma conditions "reversals" in this order have been observed. Samples with low plasma-induced-damage show the same trend as the initial R_S, as in the ECR 125 W microwave power, 0 V dc-bias data, while for heavy plasma-induced-damage, as seen in the RIE 400 V dc-bias, both shown in Table 1, the trend is opposite. The trend for heavy plasma-induced-damage is explained by the fact that the two highest doped samples have a larger fraction of the active layer thickness initially depleted (≈ 0.33), therefore, they will be the first to become fully depleted (infinite R_S). Also, the higher doped samples are more sensitive to small amounts of material removal due to lower total thickness. The lowest doped sample has the smallest fraction of the active layer thickness initially depleted (≈ 0.25) and, therefore, can still be partially conductive under plasma conditions that fully deplete the rest of the samples. Under conditions of low plasma-induced-damage, the samples will be only slightly affected from their initial resistivity, with lower R_S for the higher doped samples. Cases of intermediate plasma-induced-damage need not show a monotonic trend.

C. Anneals

When GaAs is exposed to bombardment by energetic ions, lattice or surface related damage can occur. Defects created by the plasma-induced-damage trap free carriers and account for the increase in R_S observed in this study. Annealing and removal of these defects occurs by defect diffusion and recombination at elevated temperature. For simple lattice defects, the defect removal is nearly complete by 400 °C as reported for proton implantation in GaAs[16] and seen in this work. In the case of surface related damage, the damage should be easier to repair since surface atoms have more mobility at lower temperatures due to lower activation energies for bond formation. Thus, it is plausible that under moderate plasma conditions, plasma damage can be fully recovered by modest annealing. If surface material is removed during plasma exposure, however, moderate temperature anneals will not return the lattice to its initial condition and some residual damage will persist.

Several samples have been annealed in this study to determine if the defects caused by plasma-induced-damage can be removed and low R_S recovered. R_S is plotted as a function of ECR and RIE SF_6/Ar plasma conditions (ECR microwave power and dc-bias and RIE rf power and dc-bias) for pre- and post-annealed samples (3E17 cm^{-3} doping) at 400 °C, 30 s in Fig. 5. At 125 W ECR microwave power, R_S for the pre-annealed samples increases monotonically with dc-bias and is infinite at 250 V. The post-annealed data shows significant recovery for all samples. Samples exposed to low dc-bias conditions are comparable to the pre-plasma exposure samples (6.3 kΩ/square) and at 250 V dc-bias R_S decreases from infinity to approximately 60% higher than the baseline sample R_S. A similar trend is observed at 500 W ECR microwave power, where the post-annealed samples R_S are comparable to baseline R_S. R_S for the sample exposed to 150 V dc-bias is a factor of 2 greater than the baseline which is due in part to significant loss of GaAs by physical sputtering. Post-anneal data of samples exposed to RIE plasmas show a similar trend recovering close to baseline values at 135 and 250 V dc-bias and to within 60% at 400 V. We have also evaluated the post-annealed R_S as a function of anneal temperature. The pre-annealed R_S for a sample exposed to 125 W ECR microwave power and 150 V dc-bias is infinite, however the R_S recovers to 38 kΩ/square at 200 °C, 30 s. Further increasing the anneal temperature to 300, 400, and 500 °C (30s) results in constant R_S approximately 35% higher than the baseline. R_S recovery at relatively moderate anneal conditions is consistent with a strong component of the plasma-induced-damage from damage at the surface region of Be-doped GaAs.

IV. CONCLUSIONS

The effect of plasma-induced-damage on the majority carrier transport properties of GaAs has been studied by monitoring changes in R_S of thin conducting layers using ECR SF_6/Ar, Ar, and N_2 plasmas and RIE SF_6/Ar plasmas. We speculate that plasma-induced-damage in the near surface region plays a major role in explaining the damage mechanism observed in this study and experiments are underway to verify this. Very consistent trends have been observed where R_S increases with increasing ECR and RIE dc-bias, increasing microwave power, and decreasing pressure, thus showing R_S increases as either the ion energy or ion flux increases. We have also observed that R_S is lower for samples exposed to the RIE than the ECR, possibly due to higher ion and electron densities generated in the ECR and higher pressures in the RIE. As a function of plasma chemistry, R_S is lower in SF_6/Ar plasmas than Ar and N_2 plasmas which may be related to interactions of F or S atoms with the GaAs surface. Significant recovery in R_S has been achieved at moderate anneal temperatures (200 to 500 °C) implying surface related damage since it is easily removed. Although ECR is considered a low damage plasma process and RIE is routinely used in device fabrication of high speed GaAs FETs and HBTs we have observed significant plasma-induced-damage as characterized by TLM structures indicating that parameters must be chosen carefully to optimize device performance.

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Figure Captions

Fig. 1 Sheet resistance versus dc-bias for samples exposed to the RIE SF_6/Ar plasma.

Fig. 2 Sheet resistance versus dc-bias for samples exposed to the ECR SF_6/Ar plasma at (A) 125 W and (B) 500 W microwave power.

Fig. 3 Sheet resistance versus microwave power for samples exposed to the ECR Ar plasma at (A) 0 V and (B) 50 V dc-bias.

Fig. 4 Sheet resistance versus dc-bias for samples exposed to the ECR SF_6/Ar, Ar, and N_2 plasma for (A) 1.5 E17, (B) 3.0 E17, (C) 6.0 E17, and (B) 8.0 E17 cm^{-3}.

Fig. 5 Sheet resistance versus plasma conditions (ECR microwave power/dc-bias and RIE rf-power/dc-bias) for pre- and post-anneal exposures to SF_6/Ar plasmas. The solid horizontal line at 6.3 kΩ/square represents the R_S for baseline samples which have not been exposed to a plasma.

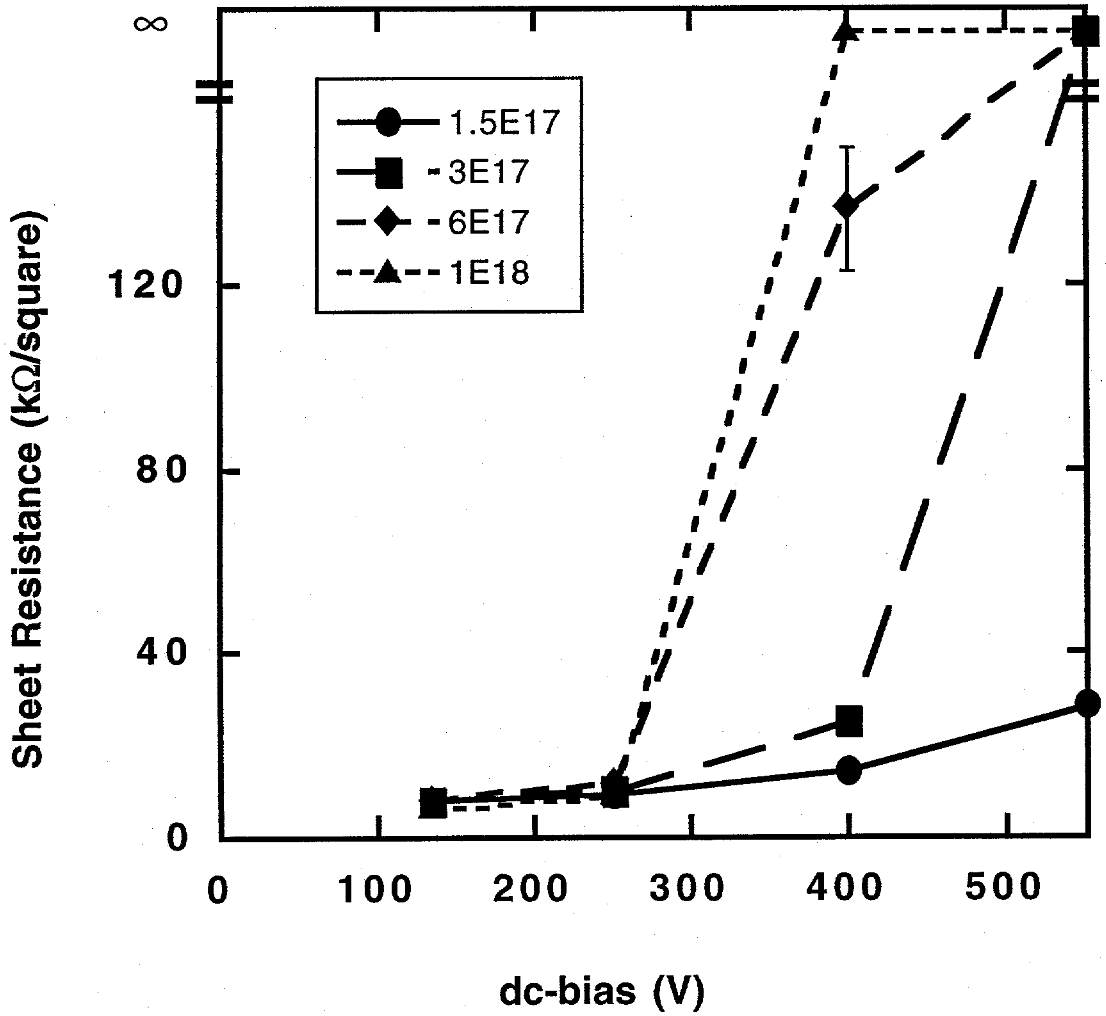

∞
120
80
40
0
Sheet Resistance (kΩ/square)
1.5E17
3E17
6E17
1E18
0
100
200
300
400
500
dc-bias (V)

Figure 1

(A)

(B)

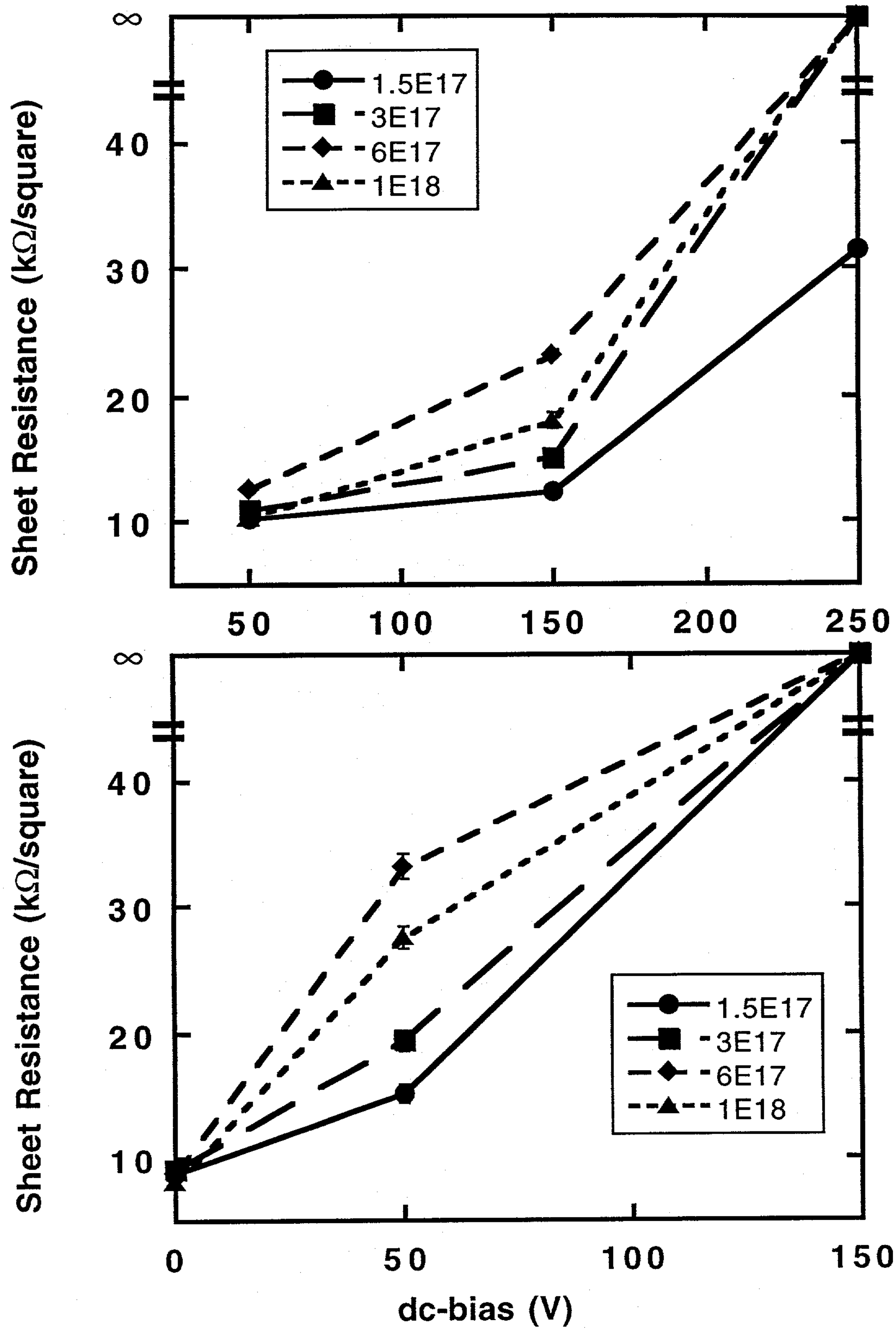
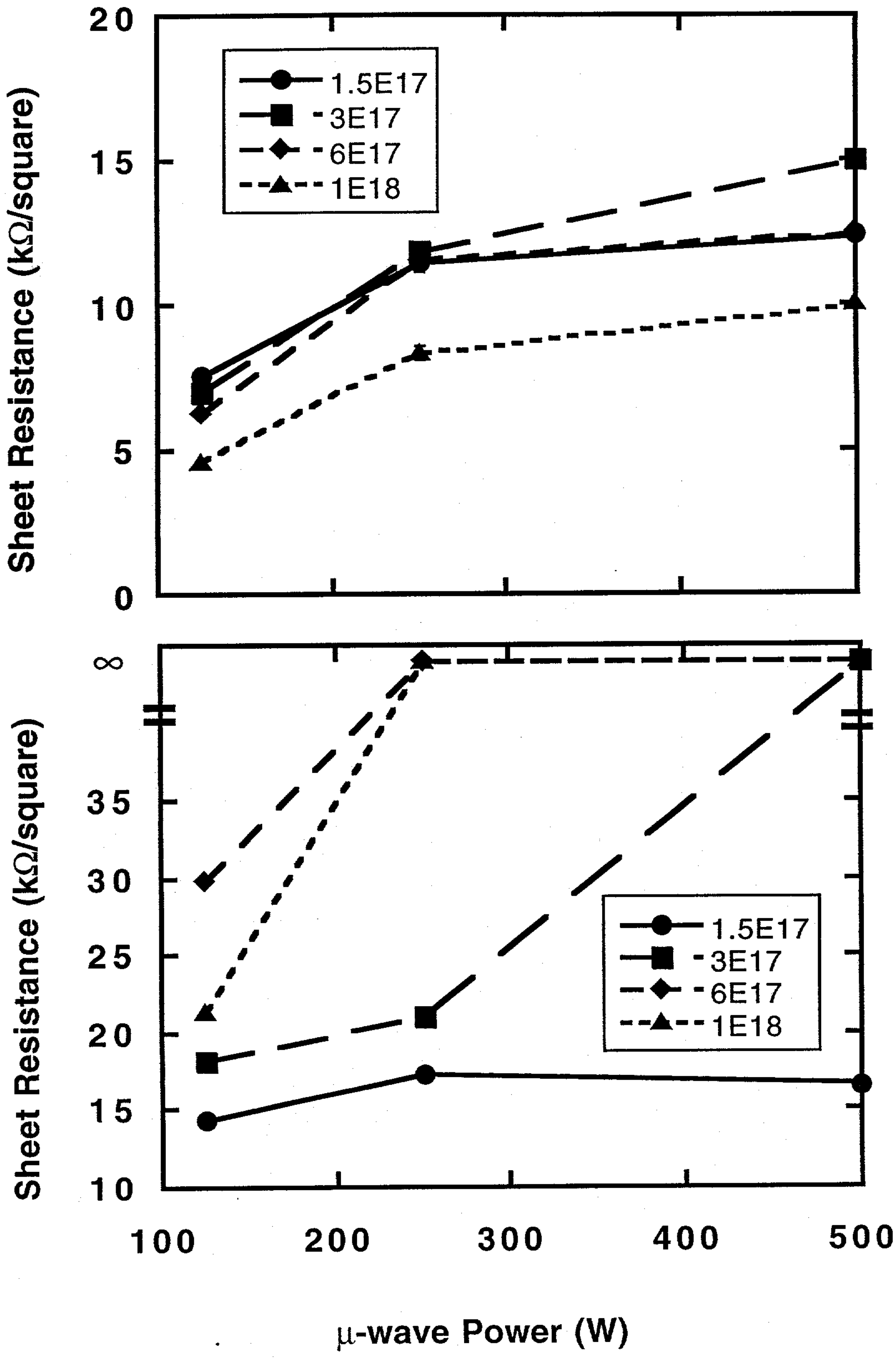

∞
1.5E17
3E17
6E17
1E18
40
30
20
10
Sheet Resistance (kΩ/square)
50
100
150
200
250
∞
40
30
20
10
Sheet Resistance (kΩ/square)
1.5E17
3E17
6E17
1E18
0
50
100
150
dc-bias (V)

Figure 2

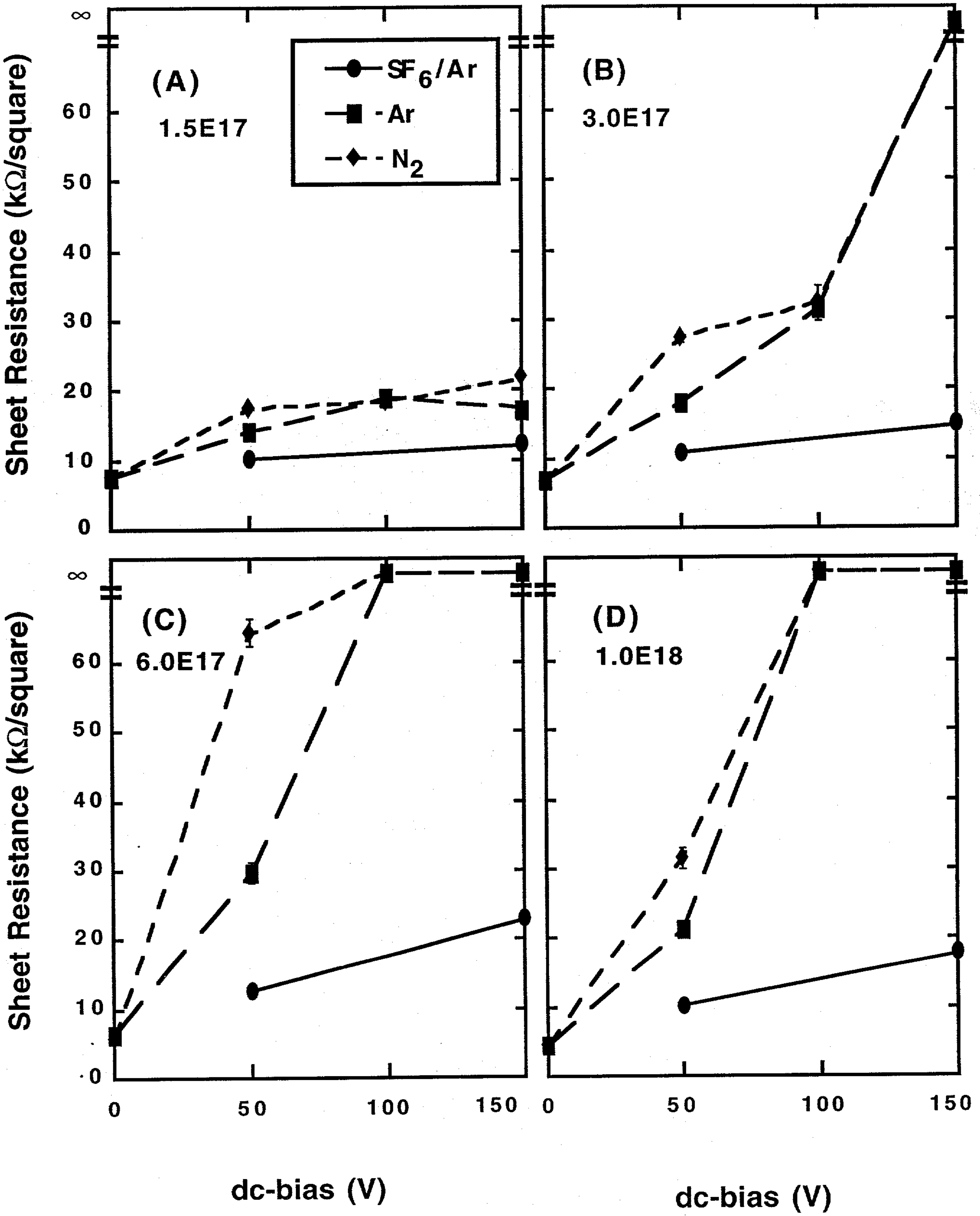
(A)

(B)



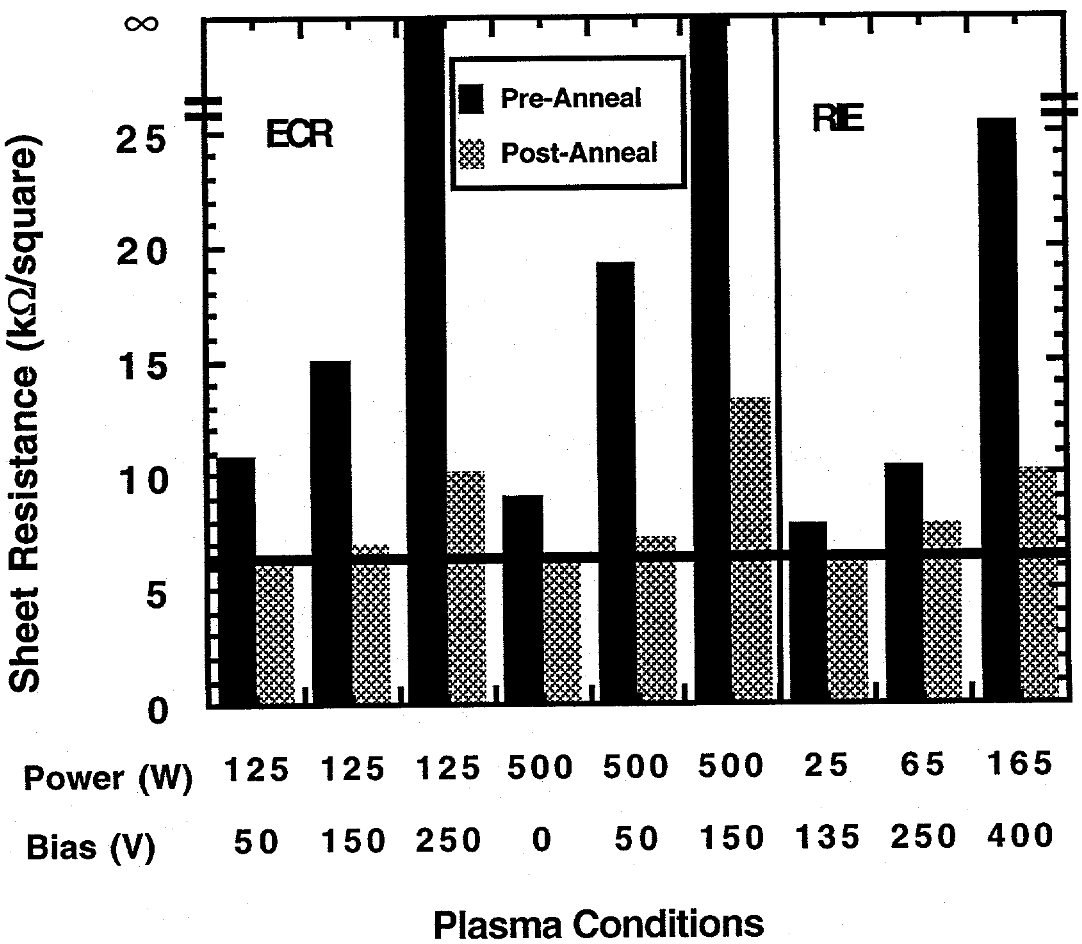
20
15
10
5
0
Sheet Resistance (kΩ/square)
1.5E17
3E17
6E17
1E18
∞
35
30
25
20
15
10
Sheet Resistance (kΩ/square)
1.5E17
3E17
6E17
1E18
100
200
300
400
500
μ-wave Power (W)

Figure 3



Sheet Resistance (kΩ/square)
∞
0
10
20
30
40
50
60
(A)
1.5E17
SF6/Ar
Ar
N2
(B)
3.0E17
(C)
6.0E17
(D)
1.0E18
0
50
100
150
dc-bias (V)

Figure 4



∞
25
20
15
10
5
0
Sheet Resistance (kΩ/square)
ECR
RIE
Pre-Anneal
Post-Anneal
Power (W) 125 125 125 500 500 500 25 65 165
Bias (V) 50 150 250 0 50 150 135 250 400
Plasma Conditions

Figure 5

	1	2	3	4
Thickness (Å), as grown	3200	1800	1150	900
Thickness (Å), after wet etch and plasma	3100	1700	1050	800
Be doping (cm^{-3})	1.5E17	3E17	6E17	1E18
R_s (KΩ/square), initial	7.12	6.57	5.9	4.72
R_s (KΩ/square), SF_6:Ar, RIE, 250V	9.14	10.4	11.8	9.55
R_s (KΩ/square), SF_6:Ar, RIE, 400 V	14.4	25.4	137	175
R_s (KΩ/square), Ar, ECR, 125µW, 0V	7.54	6.96	6.26	4.54
R_s (KΩ/square), Ar, ECR, 125µW, 50V	14.3	18.1	29.8	21.3
W_a (Å), SF_6:Ar, RIE, 250V	939	880	755	583
W_a (Å), SF_6:Ar, RIE, 400V	2022	1707	1399	1088
W_a (Å), Ar, ECR, 125µW, 0V	306	190	128	-7
W_a (Å), Ar, ECR, 125µW, 50V	2009	1476	1180	878

Table 1. Results of modeling the sheet resistance data for two RIE and 2 ECR conditions using a "damaged-layer thickness" (W_a) described in the text.