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Effects of dry etching on GaAs[a)]

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A number of dry etching techniques have been developed and their ability to produce anisotropic etch profiles has been demonstrated. In addition to etch anisotropy, an important consideration for device and circuit fabrication is whether a sample suffers radiation damage by exposure to ions, electrons, or ultraviolet light during etching. In this study we evaluate the degree of radiation damage induced in GaAs by ion-beam etching with Ar, reactive-ion etching with CF_4 and CHF_3, and ion-beam-assisted etching with Ar and Cl_2. In addition, we propose and demonstrate processing techniques which can be used after dry etching to reduce the effects of radiation damage. GaAs samples were etched under a variety of etching conditions. The degree of radiation damage caused by etching was determined by evaluating Schottky diodes fabricated on the etched surfaces and by using deep level transient spectroscopy to characterize trapping centers. It was found that the barrier heights and breakdown voltages of Schottky diodes were changed after etching. Also, an increase in the density of traps was observed. Variations in the etching conditions had a strong effect on the measured characteristics of the samples.

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I. INTRODUCTION

A number of dry etching techniques have been developed and their ability to produce anisotropic etch profiles has been demonstrated. In addition to etch anisotropy, an important consideration for device and circuit fabrication is whether a sample suffers radiation damage by exposure to ions, electrons, or ultraviolet light during etching. Contamination originating from polymer formation during etching or materials sputtered from the etching chamber can also influence device performance. Damage has been observed in GaAs after sputter etching by Yamasaki *et al.*[1] and after ion-beam etching by Chen and Wise.[2] The damage layers were estimated to be about 100 Å thick and the defects were removed by annealing at temperatures around 400 °C. However, a study by Ghandhi *et al.*[3] indicated that the depth of the damage layer was around 900 Å after ion beam etching at 100 V. A previous study by Lincoln *et al.*[4] reported an increase in trap density to $1\times10^{15}\text{cm}^{-3}$ after ion-beam-assisted etching (IBAE). In this study we evaluate the degree of damage induced in GaAs by ion-beam etching with Ar, reactive-ion etching (RIE) with CF_4 and CHF_3, and IBAE with Ar and Cl_2. The effects of etching on the electrical characteristics of GaAs were determined by evaluating Schottky diodes fabricated on the etched surfaces and by using deep level transient spectroscopy (DLTS) to characterize trapping centers. It was found that the barrier heights and breakdown voltages of Schottky diodes were changed after etching. Also, an increase in the density of traps was observed. Variations in the etching conditions had a strong effect on the measured characteristics of the samples. Techniques capable of removing the damaged layers, such as chemical etching and annealing were also investigated.

II. EXPERIMENTAL

The GaAs samples used in this study were n-type vapor phase epitaxial layers grown on n^+ substrates. The epitaxial layers had carrier concentrations around $1\times10^{16}\text{cm}^{-3}$ and were about 1 μm thick. Schottky diodes were formed on the samples by Ti–Au evaporation and the Ohmic contacts were prepared by alloying Ni–Ge–Au at 450 °C. Native oxides on the GaAs surfaces were removed by a dilute HCl dip prior to metal evaporation.

Ar ion-beam etching was performed with a Kaufman-type ion source.[5] The ion energy was varied between 250 to 1000 V. The current density was 0.25 mA/cm^2 at 250 V and 0.5 mA/cm^2 at 500 and 1000 V. The chamber pressure was maintained around 2×10^{-4} Torr during etching. Reactive-ion etching in CF_4 or CHF_3 was performed in a parallel plate reactor described elsewhere.[6] Bias voltages between 250 to 700 V were used and the chamber pressure was kept around

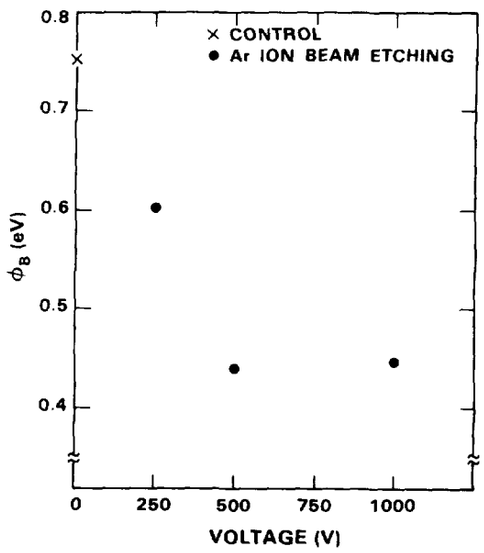

FIG. 1. Barrier height as a function of voltage used during Ar ion-beam etching. The current density was 0.25 mA/cm^2 at 250 V and 0.5 mA/cm^2 at 500 and 1000 V with a chamber pressure around 2×10^{-4} Torr.

TABLE I. Parameters deduced from I–V measurements on Schottky diodes.

Etching condition	n	ϕ_B(eV)	V_{BR}(V)
Control	1.04	0.76	38
Ar 250 V	1.06	0.60	16
Ar 250 V + PA-11 250 Å	1.07	0.73	35

1×10^{-2} Torr. For ion-beam-assisted etching,[7] Ar ions at 500 V with a current density around 20 μA/cm^2 and a Cl_2 flux equivalent to 2×10^{-3} Torr were used. The etching time was varied for different etching conditions to maintain a constant etch depth of around 2000 Å.

III. RESULTS AND DISCUSSION

A. Ar ion-beam etching

Forward and reverse I–V characteristics were measured on the Schottky diodes fabricated on GaAs surfaces after Ar ion-beam etching. Figure 1 shows the barrier height reduction as a function of ion energy. The Schottky diodes become extremely leaky as the ion energy exceeds 500 V. Table I shows the n factor, barrier height, and breakdown voltage deduced from the I–V measurements for samples before and after Ar ion-beam etching at 250 V, and for samples cleaned using PA-11 solution ($NH_4OH + H_2O_2 + H_2O$) to remove 250 Å from the surface. Auger analysis using xenon as the sputtering gas indicated that the amount of Ar present in the GaAs substrates and the penetration depth increase with ion energy. The decrease in barrier height after etching may be related to surface disorder or Ar inclusion introduced by ion bombardment during etching.[8] It has also been proposed that donorlike traps are generated by Ar bombardment which reduce the barrier height on n-type samples.[1]

The change in the effective doping concentration can be obtained from capacitance–voltage (C–V) measurements. The slope of $1/C^2$ vs V is inversely proportional to the doping density, and the intercept on the voltage axis is related to the barrier height. Figure 2 shows the change in the slope after

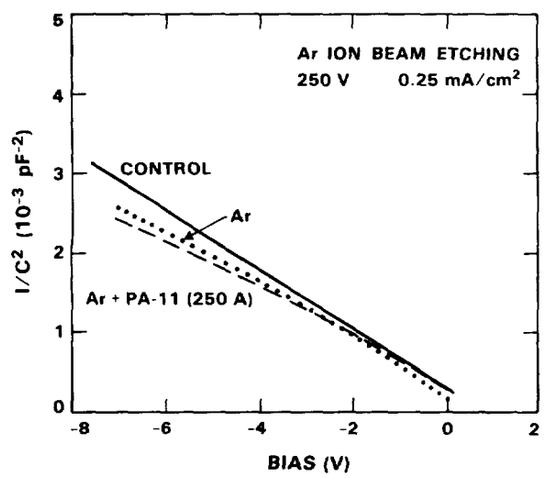

FIG. 2. Capacitance–voltage plot for a control sample, and for samples etched by Ar ion-beam etching at 250 V with and without wet etching.

Ar ion-beam etching at 250 V. This corresponds to an increase in effective doping after etching. Also shown in the figure is the result obtained after etching the top 250 Å of the surface with PA-11 solution in an attempt to eliminate ion-beam etching induced damage. The deviation of the C–V curve from the control sample indicates that residual damage remained after removing 250 Å from the surface, even though I–V measurements showed a recovery of barrier height and breakdown voltage as shown in Table I. Thus, it appears that that C–V measurements are more sensitive to changes in semiconductor characteristics such as increases in trap density or the build up of insulating layers. A complete recovery of the C–V curve is observed after removing 750 Å of the surface with PA-11 solution. The damage layer generated by Ar ion-beam etching is therefore about 750 Å and is found to be independent of ion energy in the range of 250 to 1000 V. The depth of the damage layer is greater that the Ar ion projected range. This may be related to phenomena such as channeling, vacancy migration, and enhanced diffusion induced by ion bombardment.[9]

In addition, thermal annealing was used to reduce the dry etching induced damage. The samples were annealed in N_2 at 550 °C for 30 min. Samples that were etched by Ar ion-beam etching at 250 V showed an improvement in both forward and reverse I–V characteristics. The barrier height increased from 0.60 to 0.64 V and the breakdown voltage increased from 16 to 25 V. However, the annealing was not effective in improving the I–V response for samples etched by Ar ion-beam etching at 500 and 1000 V. The diodes remained shorted with breakdown voltages less than 0.05 V. Since the degree of lattice disorder in GaAs increases with ion energy, it is expected that higher thermal energy is required for recovery of the structural damage induced by Ar ion bombardment at 500 and 1000 V. However, these higher temperatures may not be useful, since they exceed those which can be used on most metalized GaAs device wafers.

B. Reactive-ion etching

GaAs samples were reactive-ion etched in CF_4 and CHF_3 with bias voltages between 250 and 700 V. Current–voltage measurements on the Schottky diodes showed an increase in barrier height and breakdown voltage after etching at 500 V, as shown in Table II. This change in barrier height and breakdown voltage suggests the formation of a polymer film on the sample surfaces during RIE.[10] Therefore, the Schottky diodes formed on the GaAs surfaces may not be intimate metal–semiconductor contacts, but rather metal–interfacial layer–semiconductor (MIS) structures. Figure 3 shows $1/C^2$ as a function of bias voltage for samples etched in CF_4 at 700 V. The slope of the curve changes after etching

TABLE II. Parameters deduced from I–V measurements on Schottky diodes.

Etching condition	ϕ_B(eV)	V_{BR}(V)
Control	0.73	40
CF_4 500 V	0.82	50
CHF_3 500 V	0.79	62

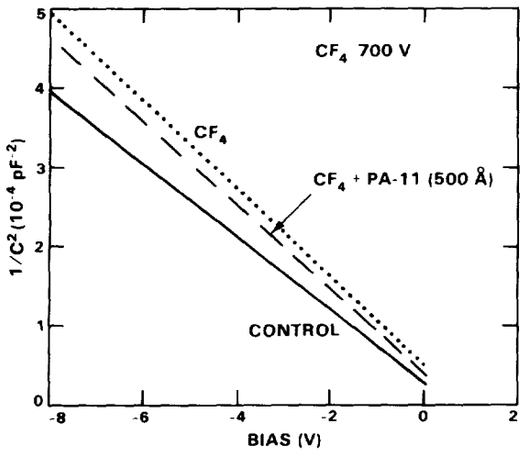

FIG. 3. Capacitance–voltage plot for a control sample, and for samples reactive-ion etched in CF_4 at 700 V with and without wet etching.

showing a decrease in measured capacitance. This may be partly due to the additional series capacitance of the polymer film. A recent study by Fonash[11] suggests that changes in $1/C^2$ vs V plot are due to the presence of interface states in the MIS structure. Lattice disorder introduced by RIE and/or imperfect bonding between the deposited polymer layer and GaAs can also cause the changes in the C–V curves. Deviation from the control sample is still observed after removing 500 Å of the GaAs surface with a wet chemical solution as shown in Fig. 3. The GaAs surfaces remained smooth after RIE and wet chemical etching.

Figure 4 shows the reduction in effective doping as a function of bias voltage used during RIE in CF_4. Effective doping concentrations were deduced from the slope of $1/C^2$ vs V plots. Deviation from the control sample doping increases with bias voltage. Also shown in the figure are the results obtained after removing 500 Å from the surface with PA-11 solution following RIE. The changes induced by RIE are not completely reversed.

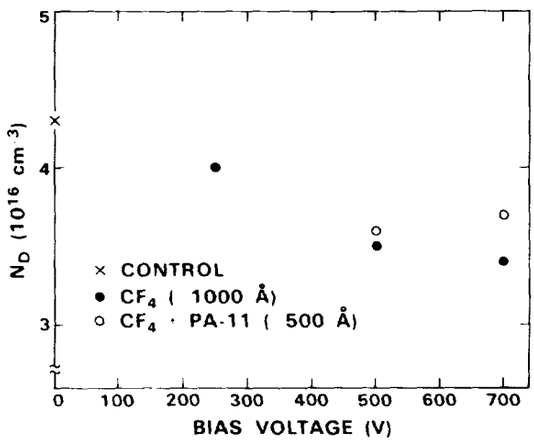

FIG. 4. Effective doping concentration deduced from $1/C^2$ plots as a function of bias voltage used during RIE in CF_4, and the effect of wet etching 500 Å with PA-11 solution.

C. Ion-beam-assisted etching

Comparison was made between samples etched by RIE in CF_4 at 250 V, RIE followed by Ar ion-beam etching at 500 V, and RIE followed by Ar ion-beam etching and IBAE in Ar and Cl_2 at 500 V. The etch depths were 100, 300, and 3300 Å, respectively. The etching sequence was similar to the processing steps used for GaAs permeable base transistor fabrication.[12] Schottky diodes fabricated directly on the etched surfaces showed similar I–V characteristics for the control and RIE + Ar + IBAE samples. Samples that were etched by RIE + Ar ion-beam etching at 500 V (the setup was identical to that for the RIE + Ar + IBAE samples except that Cl_2 was not present) became shorted with breakdown voltages below 0.05 V.

DLTS was used to detect and characterize trapping centers. In order to probe the etched surfaces, which are usually shielded by the intrinsic depletion layer under a metal contact, 0.6 μm thick GaAs layers were epitaxially grown on the etched surfaces allowing the diodes to be biased into the etched region. The growth of GaAs required cleaning the surfaces with hot H_2SO_4 solution which etches about 200 Å of the surface. The samples were also subjected to 700 °C annealing during the growth. Figure 5 shows the doping profiles after the epitaxial growth for a control sample and samples that were etched in CF_4, CF_4 + Ar, and CF_4 + Ar- + (Ar + Cl_2). Dopants were depleted from the interface between the dry etched surfaces and the epitaxial layers, especially for samples reactive-ion etched in CF_4 followed by Ar ion-beam etching. The change in doping profiles after dry etching may be due to generation of traps in the GaAs that compensate the dopants. Results from the DLTS measure-

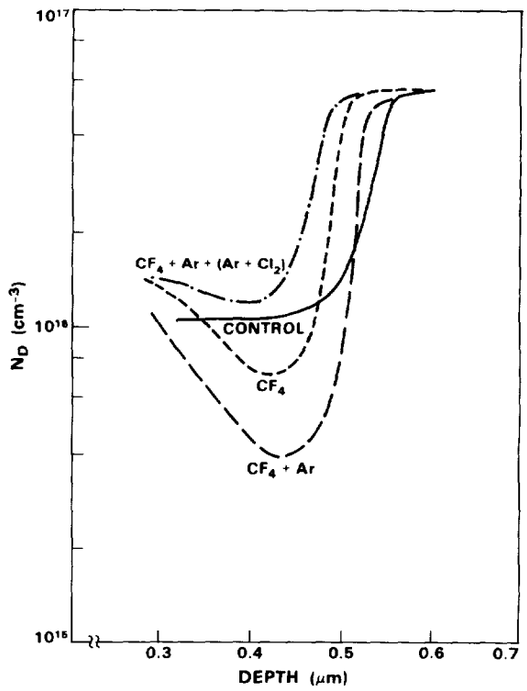

FIG. 5. Doping profiles deduced from C–V measurements for a control sample, samples etched by RIE in CF_4 at 250 V, RIE followed by Ar ion-beam etching at 500 V, and RIE followed by Ar ion-beam etching and IBAE in Ar + Cl_2.

TABLE III. DLTS measurements.

Etching condition	$N_t(10^{13}\,cm^{-3})$ Trap #1	Trap #2	Trap #3
Control	1.3		
CF_4 250 V	2.3	1.6	
CF_4 250 V; Ar 500 V	1.7	1.7	4.0
CF_4 250 V; Ar 500 V; Ar + Cl_2 500 V	1.5	2.7	

	E_a(eV)	$\sigma(cm^2)$
Trap #1	0.89	8×10^{-13}
Trap #2	0.7	3×10^{-13}
Trap #3	0.14	5×10^{-15}

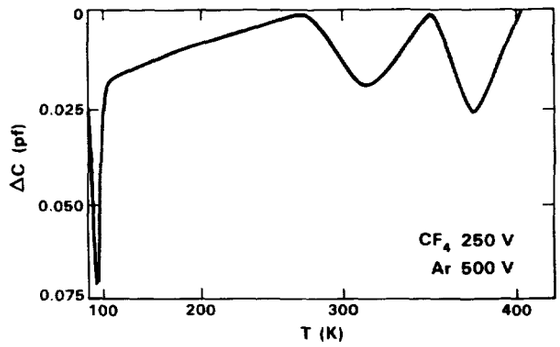

FIG. 7. DLTS signal as a function of scanning temperature for sample etched in CF_4 at 250 V followed by Ar ion-beam etching at 500 V.

ments are summarized in Table III. The control sample had a trap density around $1.3\times10^{13}cm^{-3}$. After RIE in CF_4 at 250 V, one additional trap with a concentration around $1.6\times10^{13}cm^{-3}$ was observed. When the sample was subsequently etched by Ar ion-beam etching and IBAE in Ar and Cl_2, the traps remained. However, etching the sample by Ar ion-beam etching at 500 V without the presence of Cl_2 introduced one additional trap near the conduction band edge. The DLTS signal as a function of scanning temperature is shown in Fig. 6 for samples etched in CF_4 + Ar + IBAE and in Fig. 7 for sample etched in CF_4 + Ar ion-beam etching. The results show the importance of Cl_2 in minimizing damage during IBAE. The damage generated by Ar ion bombardment during etching may be partially eliminated by the enhanced chemical etch rate in the presence of a Cl_2 flux. Further studies are needed to clarify the role of Cl_2 in damage reduction.

IV. SUMMARY

Dry etching of GaAs by Ar ion-beam etching, RIE, or IBAE has been shown to induce changes in trapping levels, barrier heights, breakdown voltages, and effective substrate dopings. The degree of damage is proportional to the bias voltage used during etching. Samples etched by Ar ion-beam etching show a reduction in barrier height and breakdown voltage, as well as additional trapping levels. The damaged layer introduced by Ar ion-beam etching can be removed by etching off 750 Å of the surface with PA-11 solution. However, most of the induced damage cannot be completely removed by thermal annealing in N_2 at 550 °C for 30 min, especially for Ar ion energies above 250 V. Samples reactive-ion etched in CF_4 or CHF_3 show an increase in barrier height and breakdown voltage after etching. In addition, the change in the slope of the $1/C^2$ vs V plot suggests the presence of a polymer layer on the GaAs surface. DLTS measurements indicate the importance of the presence of Cl_2 during IBAE to reduce the level of traps generated by Ar ion-beam etching.

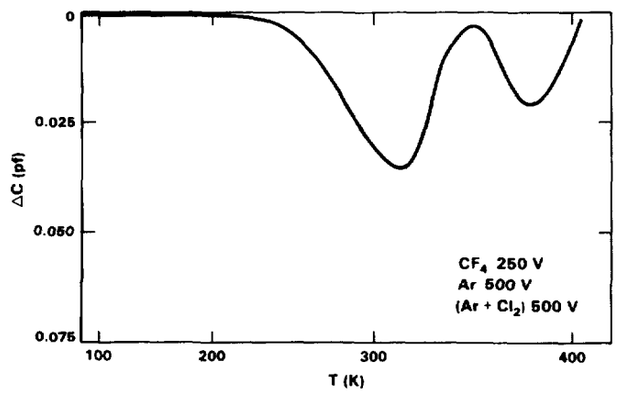

FIG. 6. DLTS signal as a function of scanning temperature for sample etched in CF_4 at 250 V followed by Ar ion-beam etching and IBAE in Ar + Cl_2.

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