REACTIVE ION ETCHING OF GaAs IN CCl_4, CCl_2F_2, and CF_4-BASED DISCHARGES

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ABSTRACT

The reactive ion etching of (100) GaAs in pure CCl_2F_2 and CF_4 discharges as well as in dilute CCl_4, CCl_2F_2, and CF_4 discharges containing 90 mole% Ar has been investigated. Anisotropic etching with removal rates of up to 0.8 μm/min have been obtained. A combination of optical emission and absorption spectroscopies were used to investigate etching mechanisms and to determine the rate limiting step in each case.

I. INTRODUCTION

Plasma-assisted etching of Si in which the plasma is used to convert inert gases such as CF_4 to reactive ion radicals (e.g., CF_3^+ and F^+) which in turn produce volatile silicon fluorides has been investigated extensively over the past several years.[1] While the detailed mechanisms of etching in various pressure regimes are still not totally understood, plasma assisted etching is presently being used in the production of Si devices requiring sub-micron feature sizes and/or anisotropic etching.[2] Plasma-assisted etching of GaAs, on the other hand, has received very little attention in the literature.[3-5]

In this paper we present some initial results on an investigation into the reactive ion etching of GaAs in CCl_2F_2 and CF_4 (CCl_4 discharges proved to be unstable for the set of operating conditions used in these experiments) as well as in dilute CCl_4, CCl_2F_2, and CF_4 discharges containing 90 mole% Ar. Etching rates have been measured as a function of gas composition and total pressure for a constant target voltage while a combination of optical emission and absorption spectroscopies were used to characterize the discharges and investigate etching mechanisms in a manner similar to studies carried out by Klinger and Greene on the reactive ion etching (RIE) of Si.[6] Finally, scanning electron microscopy was used to investigate the morphology and anisotropy of CCl_2F_2-etched features in (100) GaAs patterned with photoresist.

II. EXPERIMENTAL PROCEDURE

The reactive ion etching system used in these experiments was similar to those described previously in glow discharge optical spectrscopy (GDOS) elemental analysis,[7,8] plasma diagnostics,[8] and RIE studies.[5,6] A schematic diagram of the etching chamber and the optical system is shown in Figure 1. The chamber was constructed of pyrex in the shape of a cross. A parallel plate reactor with Al electrodes formed one axis. Quartz windows with > 95% transparency over the spectral range studied, from 200 nm to 800 nm, were mounted along the optical axis. Separation of the windows from the discharge prevented any measurable loss in optical transmission during runs lasting up to several hours. The inside of the chamber was coated with Ni to

prevent chemical attack of the walls by the etching gases. The GaAs targets used in these experiments were (100) oriented, 1.9 cm diameter, wafers attached to the water cooled cathode with an Ag-based epoxy.

The system base pressure was 2.7×10^{-3} Pa (2×10^{-5} Torr) using a trapped diffusion pump. Etching gases were pre-mixed in a differentially pumped buffer volume to obtain the desired composition at a total pressure of $\sim 1 \times 10^{5}$ Pa (760 Torr). The total etching gas pressure P was then adjusted by varying the flow rate into the reactor while maintaining a constant pumping speed. P was monitored using a capacitance monitor. The target to counter-electrode spacing was 4 cm and the target voltage was -3.0 kV.

The optical detection system shown schematically in Figure 1 allowed both optical emission and absorption studies to be carried out. A set of lenses and slits placed along the optical axis between the reactor and the spectrometer focused the spectrometer on a narrow region of the discharge, $\sim$0.5 mm in width, immediately in front of the target. The reactor could also be translated orthogonal to the optical axis allowing the discharge to be profiled. The optical signal from the discharge was dispersed in a 0.75 m grating spectrometer and detected using a high speed photomultiplier and photon counting system capable of linear operation over the range from < 100 cts/s to $> 10^{7}$ cts/s. In the absorption mode, the emission from hollow cathode lamps used as atomic line sources was mechanically chopped in synchronous with a lock-in amplifier in the detection circuit to eliminate the dc emission signal from the discharge.

III. EXPERIMENTAL RESULTS

Surface chemistry reaction paths during the reactive ion etching of a compound such as GaAs are necessarily complex. Adsorbed gas species must form volatile reaction products with both Ga and As and, depending on the experimental conditions, the reaction and desorption rates with either sub-lattice species could provide the rate limiting step for the overall etching process. In the present case, the fluorides of As are volatile while GaF_3 is a solid which sublimes at high temperatures. On the other hand, both $AsCl_3$ and $GaCl_3$ have reasonably high vapor pressures at room temperature.

Figure 2 shows measured GaAs etching rates R as a function of gas pressure P for pure CCl_2F_2 and pure Ar discharges. In both cases, R increased with increasing P, but the etch rate in CCl_2F_2 was more than an order of magnitude higher than in Ar. The etching mechanism in the Ar discharge was completely due to physical sputtering and atomic absorption spectroscopy indicated the presence of large concentrations ($\sim 10^{10}$ cm^{-3} at P = 40 mTorr) of sputtered atomic Ga and As species immediately in front of the target surface. However, during etching in CCl_2F_2 discharges, no measurable Ga or As atomic absorbance was observed adjacent to the target (although absorbance was obtained further out in the discharge as will be discussed) even though R was, for example, a factor of 20 larger at P = 40 mTorr.

The above results provide some evidence that simple physical sputtering is not a primary etching mechanism in CCl_2F_2 discharges since for the average ion impact energies used in these experiments, a few hundred eV,[9] the primary sputtered species from a GaAs target are neutral Ga and As atoms rather than molecules.[10] In fact, we observed that adding just 10 mole% CCl_2F_2 to an Ar discharge maintained at a total pressure of 40 mTorr reduced the near-target Ga and As absorbance signals to zero while increasing R by more than a factor of three. By comparison with results for a pure Ar discharge,

this means that less than 0.1% of the etched material was removed in the atomic state.

The etch rate in pure CF_4 discharges at P = 40 mTorr decreased to 310 nm/min from a value of 760 nm/min for CCl_4. Accounting for differences in target current, the etch rate per unit target power, R', was 13.8 nm/min-W for CF_4 compared to 33.8 nm/min-W for CCl_4. The near-target atomic absorption results again indicated no significant ejection of atomic As during etching, however $\sim$ 1% of the Ga was removed as atomic species. Both the decreased etch rate and the increase in atomic Ga ejection during etching suggest that the rate limiting step in the RIE of GaAs in CF_4 discharges is the removal of Ga and non-volatile GaF_3. Physical sputtering in this case would be expected to play a more active role in the etching process.

Figure 3 shows optical emission spectra in the range from 200 to 400 nm from the near-target region of the discharge during the etching of GaAs in (a) Ar, (b) CCl_2F_2, and (c) CF_4. In addition to the Ga and As emission lines which were present in all spectra, strong atomic emission from C, Cl, and F (the primary F peak at 656.9 nm is not shown in Figure 3) as well as molecular emission bands due to halocarbon radicals were observed in the reactive discharges. The broad continuum centered near 305 nm was only observed in CF_4-based discharges and we have previously assigned it to be due primarily to closely spaced CF_3 emission bands.[6]

The emission intensities of the resonant Ga (287.4 nm) and As (197.2 nm) lines were considerably reduced in the reactive discharges compared to the pure Ar case even though the etch rates were more than an order of magnitude larger. In fact, the only reason that the Ga and As emission lines from the reactive discharges are visible at all on the scale shown in Figure 3 is the increased excitation probability. Another point to note is that the ratio of the Ga/As emission intensities is approximately an order of magnitude higher in the reactive discharges than in Ar. These results taken together are a further indication that there is considerably less sputtering of atomic Ga and As species in the reactive discharges, but that of this small amount the fraction of Ga is much larger than that of As.

Scanning electron microscopy (SEM) studies of patterns etched in GaAs using photoresist masks showed no indications of under cutting. Vertical step heights of up to 2 μm were etched in CCl_2F_2 using test patterns with feature sizes ranging from 20 to 10 μm. The bottom of the etched region exhibited a smooth terranced morphology along crystallographic directions.

Investigations of the reactive ion etching of GaAs were also carried out in dilute 10 mole% CCl_xF_{4-x} + 90 mole% Ar discharges. The etch rate per unit target power R' was considerably larger in the dilute reactive discharges (29.2, 25.8, and 22.0 nm/min-W for dilute CCl_4,CCl_2F_2, and CF_4 discharges, respectively) than in the pure Ar discharge (13.3 nm/min-W), all operated at a pressure of 40 mTorr. Moreover, in the reactive discharges, R' increased as the Cl concentration increased. No As absorbance was observed immediately in front of the target surface in any of the dilute reactive discharges. However, significant Ga absorption, approximately 25% of that observed in pure Ar (4.5% if the absorbance is normalized to the etching rate), was observed in the dilute CF_4 discharge. Ga absorbance was not detectable adjacent to the target in dilute CCl_2F_2 and CCl_4 discharges.

Optical emission spectra from the near-target region of the discharge showed that the Ga/As resonant emission intensity ratio was approximately twice as

as large in the dilute CF_4 discharges as in dilute CCl_4 and CCl_2F_2. In the latter cases, the ratio was in turn approximately twice as large as in pure Ar. Large atomic C emission peaks were also observed in the dilute halocarbon discharges, with the largest intensity recorded during etching in dilute CCl_4.

In order to characterize the target surface composition during steady state etching, a series of in-situ optical emission experiments, similar to those carried out for Si etching in CF_4,[6] were undertaken. In these experiments, steady state etching discharges were first established. The discharges were then extinguished, the etch gas valved off and pumped out, and the reactor backfilled with pure Ar to a pressure of 40 mTorr. An Ar discharge was then established with V_T = -3.0 kV, and near-target C, Ga, As, Cl, and F peak intensities were monitored as a function of time as during sputtering of the previously etched targets. The etched samples were not air-exposed. Figure 4 shows measured C (247.8 nm) intensities as a function of sputtering time. The C emission intensity from an unetched air-exposed GaAs wafer is also shown for comparison. A carbon acculation layer was clearly present on all etched samples during steady state etching with the total amount of carbon increasing with increasing Cl/F ratio in the etch gas.

IV. DISCUSSION

The results presented in section III show that rapid non-isotropic reactive ion etching of GaAs can be achieved in CCl_4, CCl_2F_2, and CF_4-based discharges. The optical emission and absorption studies demonstrated that even in the dilute 10% halocarbon + 90% Ar discharges, atomic sputtering was not the primary etching mechanism for GaAs. Ion bombardment did, however, play several important roles in the overall etching process, such as providing directionality of etching, the dissociation and removal of non-volatile GaF_3, and the removal of deposited carbon from the GaAs surface.

Direct evidence was presented for the accumulation of carbon on the target surface during the reactive ion etching of GaAs. Monitoring optical emission intensities as a function of time after initiation of the discharge showed that the rate limiting step for achieving steady state etching was the time required to accumulate a steady state carbon coverage. Carbon deposition occurred due to impact dissociation of halocarbon ions (CCl_x^+ and/or CF_x^+, depending on the etch gas) and the dissociative chemisorption of halocarbon radicals (CCl_x and/or CF_x). At steady state, the carbon deposition rate was balanced by the carbon removal rate due to both physical sputtering and the formation of volatile halocarbon species through recombination at the target surface. Under the conditions used in the present experiments, a steady state etch rate was obtained in less than 1 sec for the pure etch gases and less than 20 sec for the dilute gases.

The equivalent thickness of the carbon overlayer, in the case of the dilute etch gases, was found to be largest in CCl_4 and smallest in CF_4 discharges. CF_4-based discharges also resulted in the lowest etching rates. Both effects, low R and high C coverage in CF_4, were due to the absence of volatile Ga-containing species in this system. The overall etch rate in CF_4-based discharges was limited by the rate of sputtering of Ga and GaF_x. The removal of Ga or gallium fluoride radicals by sputtering, rather than by desorption of volatile gallium halide, freed some active halogen (i.e., fluorine) species which were available to react instead with adsorbed carbon, form a volatile halocarbon, desorb, and reduce the steady state carbon coverage. In CCl_4-based discharges, on the other hand, the concentration of free halogen species available at the surface was reduced since more halogen (chlorine, in this

case) was involved in the etching process through the formation of volatile $GaCl_3$.

The atomic absorption results showed that in all cases investigated in these experiments, sputtering of atomic As accounted for less than 0.1% of the total As removed. Measurements of absorbance vs distance away from the target, however, indicated that atomic As was produced in the discharge due to dissociation of desorbed arsenic halide species. Since the probability of recombination in the gas phase is low, the dissociation reaction provides another source of active halogen species for etching. The arsenic produced in the gas phase is simply pumped away.

REFERENCES

(1) See for example, C.M. Melliar-Smith and C.J. Mogab, "Plasma Assisted Etching Techniques for Pattern Delineation," in Thin Film Processes, ed. by J.R. Vossen and W. Kern, Academic Press, New York (1978).

(2) R.W. Kirk, "Applications of Plasma Technology to the Fabrication of Semiconductor Devices," in Techniques and Applications of Plasma Chemistry, ed. by J.R. Holahan and A.T. Bell, John Wiley & Sons, New York (1975).

(3) E.R. Hu and R.E. Howard, Appl. Phys. Lett. 37, 1022 (1980).

(4) G. Smolinsky, R.P. Chang, T.M. Mayer, J. Vac. Sci. Technol. 18, 12 (1981).

(5) R.E. Klinger and J.E. Greene, Appl. Phys. Lett. 38, 620 (1981).

(6) R.E. Klinger and J.E. Greene, "Glow Discharge Optical Spectroscopy Studies of the Reactive Ion Etching of Si," Plasma Processing, ed. by R.G. Frieser and C.J. Mogab, The Electrochemical Society Proceedings, Volume 81-1, New Jersey (1981).

(7) J.E. Greene, F. Sequeda-Osorio, and B.R. Natarajan, J. Appl. Phys. 46, 2701 (1975).

(8) J.E. Greene, J. Vac. Sci. Technol. 15, 1718 (1978).

(9) W.D. Davis and T.A. Vanderslice, Phys. Rev. 131, 219 (1963).

(10) J. Comas and C.B. Cooper, J. Appl. Phys. 38, 2956 (1967).

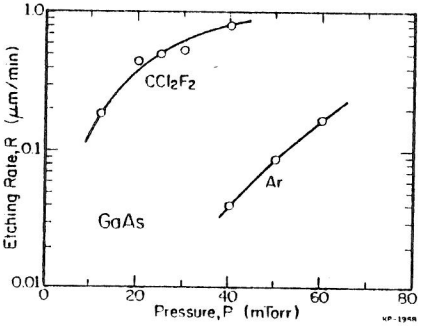

Figure 2. GaAs etching rate vs etching gas pressure for pure CCl_2F_2 and Ar discharges. The target voltage was -3.0 kV.

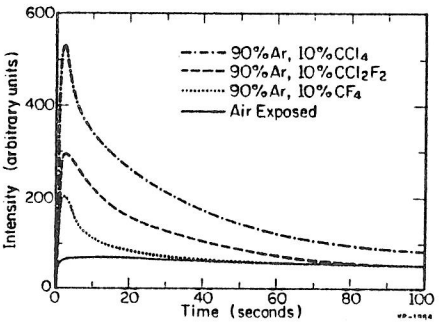

Figure 4. Near-target atomic C (247.8 nm) emission intensities as a function of time during Ar^+ sputtering of a GaAs wafer which had previously been reactively ion etched to steady state.

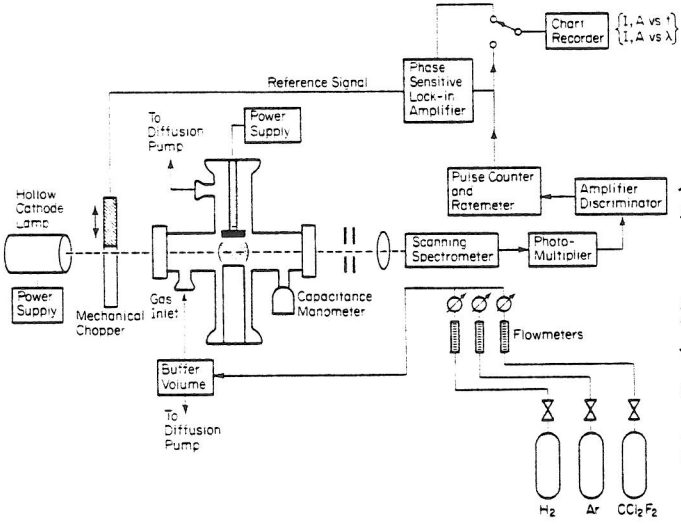

Figure 1. Schematic diagram of the reactive ion etching chamber with optical emission and absorption spectroscopy systems for in-situ analysis.

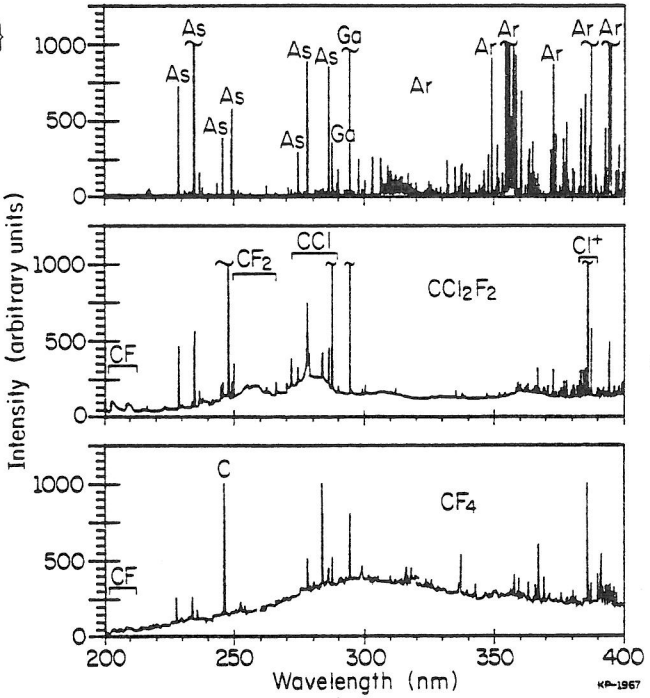

Figure 3. Near-target optical emission in the wavelength range from 200 to 400 nm for Ar, CCl_2F_2 and CF_4 discharges during etching of GaAs. The target voltage was -3.0 kV and the total pressure was 40 mTorr.