Magnetic field effects on cylindrical magnetron reactive ion etching of Si/SiO₂ in CF₄ and CF₄/H₂ plasmas

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Etching of Si and SiO₂ has been investigated as a function of magnetic field strength in a radiofrequency cylindrical magnetron discharge using CF₄ and CF₄/H₂ gas mixtures. Si and SiO₂ etch rates increased with increasing magnetic field strength by a factor as large as 5 at a given power density. Futher increases in magnetic field strength, though, decreased etch rates in both CF4 and CF₄/H₂ plasmas. The density of CF, CF₂, and F radicals, inferred from optical emission intensities, increased continuously as a function of magnetic field strength. Ion densities, measured by electrical probes, increased by a factor of ≈15 as the magnetic field strength was increased from 0 to 250 G in a CF₄ discharge (0.45 W/cm²). However, the self-bias voltage on the powered electrode decreased rapidly with increasing magnetic field, from ~1 kV at 0 G to almost 0 V at 250 G. The maximum etch rates occurred at an intermediate magnetic field strength where the self-bias voltage was between 25 and 50 V, which corresponds to conditions which maximize both the effectiveness of ion bombardment and ion density. With these conditions, the polymer thickness formed on the Si was a minimum and C/F ratio on the surface was a maximum. Highly anisotropic etching was also obtained near these conditions.

I. INTRODUCTION

Magnetrons have been used for number of years as sputtering sources as a result of their unique ability to deposit over large areas in short processing times. 1,2 Recently, the use of magnetrons has been extended to reactive ion etching³⁻⁵ with a goal of utilizing the enhanced rates of ionization and dissociation one obtains in a magnetron discharge.

Various geometries have been investigated as methods to enhance the ion and radical densities in discharges used as a reactive ion etching sources. Some of these are planar diode discharges with a magnetic field applied perpendicular to the electric field,^{5,7} planar magnetron discharges,^{3,8} cylindrical magnetron discharges, 9-12 and other novel geometries. 13,14 The first application of rf magnetron discharges to Si/SiO₂ etching was reported by Horiike et al.3 in 1981 who obtained high etch rates and good selectivity using CHF3 in a planar geometry. In experiments conducted by Hinson et al.4 using a cylindrical geometry, Si/SiO₂ etch rates of 3000 Å/min were obtained with $CF_4 + (H_2/O_2)$ gas mixtures. A selfbias voltage of < 200 V developed in their apparatus with a magnetic field strength up to 200 G. The chemistry of rf cylindrical magnetron discharges (200 G) has been investigated by Bright et al. 12 for $CF_4 + (H_2/O_2)$ gas mixtures using mass and optical spectroscopy. They also studied the contamination of the etched surfaces using x-ray photoelectron spectroscopy (XPS). In many of the previous works permanent magnets were used. As a result, the effect of magnetic field strength on the processing parameters has not been systematically investigated.

In this paper we report on the effects of the magnitude of the magnetic field on the plasma chemistry of radio-frequency CF₄/H₂ cylindrical magnetron discharges. We also report on the dependence of the etch rate and etch profiles of Si and SiO₂ on magnetic field strength. Langmuir probes and optical emission spectroscopy were used to study plasma parameters. Etched Si and SiO2 surfaces were examined by

Auger electron spectroscopy (AES) to study the residue of the etched Si surface as a function of magnetic field strength.

II. EXPERIMENTAL APPARATUS AND METHODS

The experimental system is shown schematically in Fig. 1. It is functionally the same as that used to characterize magnetron discharges in noble gases, and is described in detail elsewhere. The exception to the prior description is that the inner cylindrical electrode, formerly made of stainless-steel, was replaced by one made of anodized aluminum. The new inner electrode has four flat sides and end flanges which aid in trapping electrons. The diameter of the inner electrode is 100 mm and the area of the electrode exposed to the plasma is 670 cm². The flat sides of the inner electrode were used as specimen holders. Two electromagnets were located outside and around the chamber. The magnets were supported by carbon steel to enhance the magnetic field strength and to give a uniform magnetic field inside the chamber. Details of the design of the electromagnets are described elsewhere. 15 The field strength we studied was varied from 0 to 250 G and was uniform inside the chamber to $\pm 15\%$ and on the electrode surface to \pm 5%. The samples studied in this experiment were single-crystal N-type Si(100) with bulk resistivity of 5 to 20 Ω cm. To study the etching of SiO₂, 1.5- μ mthick wet oxide layers were grown in a furnace. The Si and SiO₂ samples were masked using Shipley 1450J photoresist and a step analyzer (Tencor Instruments Alpha-step 100) was used to measure the etch rates. When using scanning electron microscopy (SEM) to study the etch profiles, Cr masks were used instead. An AES system (Physical Electronics) was used to study the depth of polymer layer and to study species contributing to surface contamination of the etched Si.

An electrostatic probe was used to measure ion densities as a function of magnetic field strength. The probe was made of a cylindrical tungsten tip 0.25 mm in diameter × 5 mm

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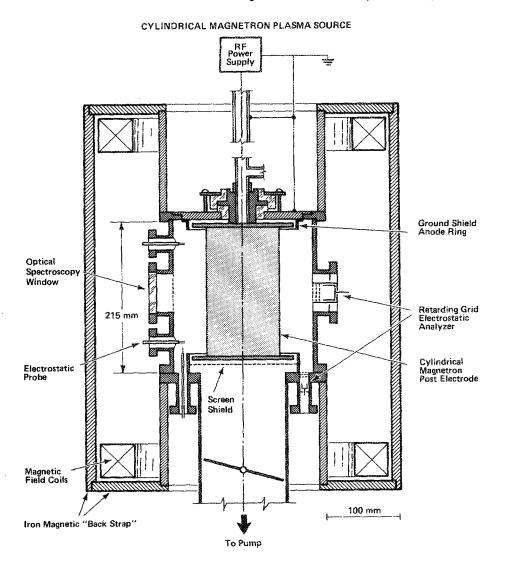


FIG. 1. Schematic of the experimental apparatus

long. The tip was supported by a tubular quartz insulator which shielded the tip and prevented shorting.

The system was evacuated to $< 1 \times 10^{-6}$ Torr by a diffusion pump before pure CF₄ or CF₄/H₂ mixtures were introduced. The pressure was varied from 1 to 15 mTorr and the power density (13.56 MHz) on the anodized electrode was varied from 0.45 to 1.2 W/cm². A high-voltage, high-impedance probe (Tektronix model P6015) was used to measure the peak-to-peak voltage and the cathode bias voltage.

An optical multichannel analyzer having an intensified diode array (Princeton Instrument IRY-700) was interfaced to a microcomputer (IBM PC/AT) to study the optical emission of the plasma. The light to the spectrograph (150 g/mm) was focused through a quartz window located at the middle of the chamber. Argon actionometry 16,17 was used to estimate F atom densities from optical emission intensities measured for various conditions.

III. ETCH RATES AND PLASMA PROPERTIES VERSUS MAGNETIC FIELD

Etch rates for Si and SiO_2 using CF_4 are shown in Fig. 2(a) for different power densities as a function of magnetic field strength. Etch rates of many 1000s Å/min were obtained with the application of magnetic field as previously

noted by other researchers in different magnetron etching systems. However, the etch rates did not necessarily increase monotonically with increasing magnetic field. At a power density of 0.45 W/cm², the Si and SiO₂ etch rates both exhibit a maximum near 60 G, decreasing to a nearly constant value at higher magnetic fields. The magnetic field value at which the maximum etch rate was obtained moved to higher values with higher discharge power densities. Etch rates for different CF₄/H₂ mixtures are shown in Fig. 2(b) for a fixed power density of 0.45 W/cm². The same dependence of etch rate on magnetic field strength is obtained as in Fig. 2(a). The magnetic field strength at the maximum etch rate has a weak dependence on gas mixture, moving to lower magnetic field with increasing hydrogen fraction. The selectivity of SiO_2 over Si with CF_4/H_2 was generally < 3 and was not a strong function of magnetic field strength. However, in CF₄ plasmas, the selectivity was generally lowest when the Si etch rate was highest. As hydrogen was added to the CF₄ plasma, the etch rates for both Si and SiO₂ decreased. The selectivity of SiO₂ over Si increased with increasing H₂ as we expect in analogy to results obtained by reactive ion etching (RIE). However, even though hydrogen was added to a mole fraction of more than 50% (not shown) etching of Si could not be prevented by polymerization as is obtained in conventional RIE.

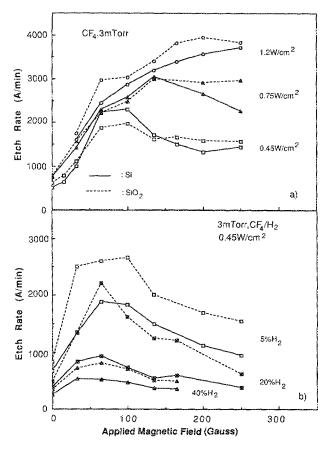


Fig. 2. (a) The effect of magnetic field strength and power deposition on the etch rates of Si and SiO_2 in CF_4 (3 mTorr). (b) The effect of magnetic field strength on the etch rates of Si and SiO_2 for different CF_4/H_2 mixtures (3 mTorr, 0.45 W/cm²).

When optical emission spectra were measured for CF₄ discharges, all of the emission lines for CF2, CF, and F increased approximately the same fractional amount when the magnetic field was increased. The change in the emission intensities, though, do not necessarily represent the change in radical densities in the plasma due to differences in excitation and quenching rates. 16 To estimate the radical densities, atomic F emissions (703.7 nm) were normalized by the emission intensity of Ar at 750.4 nm, which was added to a mole fraction of 3%. Figure 3 shows the normalized F atomic emission as a function of magnetic field strength for several CF₄/H₂ gas mixtures at 3 mTorr of total pressure and at 0.45 W/cm² power density. The F atom density inferred by this normalization increased with increasing magnetic field but decreased with hydrogen addition due to smaller mole fraction of CF₄ and the formation of HF. The fractional increase in F atom density at 40% H₂ was only nominal compared to the smaller dilutions. The relative ion densities measured in the pure CF₄ discharge are also shown in Fig. 3. The ion densities were measured ~1 cm from the inner electrode on the middle plane of the chamber. The ion density increased from 6.6×10^9 to 1.1×10^{11} cm⁻³, an increase of ~15 times in increasing the magnetic field to 250 G, commensurate with the increase in F atom density.

The measured bias voltages for the conditions for Fig. 2 are shown in Fig. 4. The bias voltages decreased exponentially as the magnetic field strength increased. The bias voltage

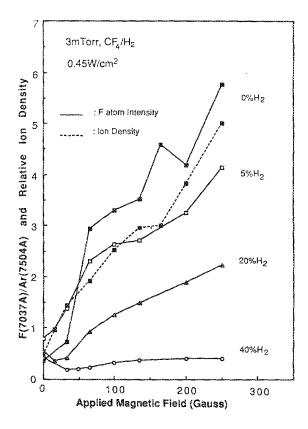


FIG. 3. Relative F atom densities estimated from Ar actinometry for different CF_4/H_2 mixtures (3 mTorr, 0.45 W/cm²). Dashed line is the relative ion density (0% H_2) measured with a Langmuir probe.

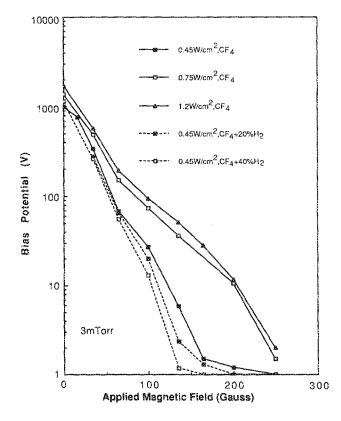


FIG. 4. Self-bias voltages as a function of magnetic field for the conditions of Fig. 2.

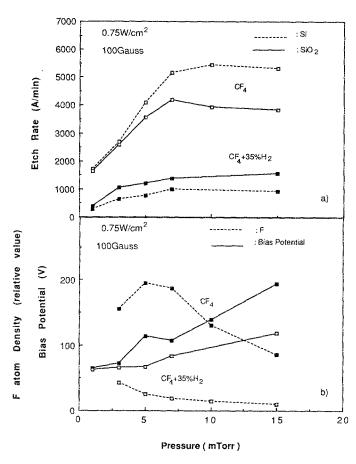


Fig. 5. (a) The effect of gas pressure on the etch rates of Si and SiO₂ in CF₄ and CF₄ + 35% $\rm H_2$ discharges. The etch rates were measured at a power density of 0.75 W/cm² and magnetic field of 100 G. (b) The F atom density measured by Ar actinometry and the self-bias voltages for same conditions.

decreased with increasing H_2 fraction in CF_4/H_2 discharges but the change was small compared to that caused by magnetic field. Bias voltage at a particular magnetic field increased with increasing power deposition in the plasma.

The etch rates of Si and SiO_2 increased with increasing pressure up to nearly 7 mTorr, and then saturated or slightly decreased with further increase in pressure. These trends are shown in Fig. 5(a) for CF_4 and $CF_4 + 35\%$ H_2 at 100 G and a power deposition of 0.75 W/cm². In Fig. 5(b) the measured self-bias voltages and F atom densities, estimated by argon actionometry, are shown for these conditions. For both CF_4 and $CF_4 + 35\%$ H_2 discharges, F atom density decreased with increasing pressure while the bias voltage increased.

The ratio of C to F contained in the etched Si surfaces, as measured by AES, and the depth of the polymer layer is shown in Fig. 6. The C/F ratio [Fig. 6(a)] has a peak near 60 G in CF₄ (3 mTorr, 0.45 W/cm²) which corresponds to the conditions at which the maximum etch rates were obtained [see Fig. 2(a)]. At these conditions, the minimum polymer thickness is also obtained [Fig. 6(b)].

IV. DISCUSSION

The introduction of the magnetic field perpendicular to the electric field causes the electrons emitted from the elec-

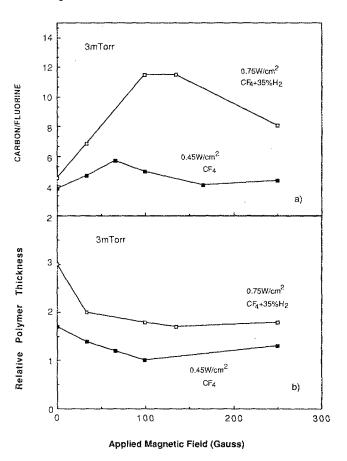


FIG. 6. (a) The ratio of carbon to fluorine on the etched silicon surface measured by AES. (b) Thickness of the polymer layer estimated by AES.

trode surface to have helical motions and a drift in the direction of $\mathbf{E} \times \mathbf{B}$, nominally parallel to the cathode surface. By making the $\mathbf{E} \times \mathbf{B}$ current' closed on a circle concentric with the cathode, the electrons are trapped near the cathode thereby reducing their rate of loss from the plasma. Therefore, more ionizations and dissociations are expected per unit power deposition compared to the case without the appropriately applied magnetic field. The increase in the ion densities and radical densities shown in Fig. 3 demonstrates the trapping effect of the magnetic field on electrons. Another consequence of operating in the magnetron mode is a decrease in electron mobility perpendicular to the magnetic field, while having less of an effect on ions. This relative decrease of the electron mobility compared to ions reduces the need for a dc self-bias. The dc self-bias voltages on the powered electrode therefore decreases as the magnetic field strength is increased, as shown in Fig. 4. The commensurate increase of ion density and F atom density at low H₂ dilution (see Fig. 3) indicates that the larger F atom density is due simply to increased electron impact dissociation of CF₄. The saturation of F atom density with increasing H₂ could result both from the cited depletion of F by formation of HF or depletion of CF₄ by electron impact dissociation. There appears to be no evidence for a loss of the magnetron effect with high dilution of CF_4 by H_2 .

The dependence of $\mathrm{Si/SiO_2}$ etch rates on applied magnetic field (Fig. 2) is likely explained by the increasing radical density and decreasing bias voltage. The increase in the den-

sity of CF₃ and F radicals, and in the ion density with increasing magnetic field increases the chemical components of the Si and SiO₂ etch rates. The increase is sustained until such time that the lower energy of ions bombarding the substrate resulting from the decrease in the dc self-bias is insufficient to activate the etching process. Below this critical ion energy (i.e., at higher B fields), etching rates decrease. Therefore, there is a maximum in the etch rates where the two effects are compensating. When increasing power, the maximum in the etch rate moves towards higher magnetic field in such a manner as to maintain the bias voltages at maximum etch rate in the range 25-50 V (compare Figs. 2 and 4). There appears then to be a threshold energy required for the ions to promote surface reactions effectively. The small decrease in the magnetic field strength at the maximum etch rate upon dilution with H_2 [see Fig. 2(b)] is a consequence of the reduction in dc bias with dilution (see Fig. 4) at fixed magnetic field. Also, the lighter H_2^+ ions may be less effective in activating the etching process. Higher ion energies are therefore required.

Magnetrons are generally operated at a low pressure, 1–10 mTorr, because scattering at higher pressures reduces the efficiency of confinement of the electrons. The rate of ionization is also reduced. The observed decrease in etch rate with increasing pressure [Fig. 5(a)] may be attributable to these effects. Another cause may be that there is a higher probability of gas phase recombination reactions which reduce the radical density. The increase in the dc self-bias voltage and decrease in F atom density with increasing pressure [Fig. 5(b)] suggest that the electron trapping efficiency is indeed being reduced and the magnetron effect is being lost.

Magnetic field strengths that provide the highest etch rates also had the smallest polymer layer thickness and the highest C/F ratio, as shown in Fig. 6. The fact that the polymer thickness was a minimum and etch rate a maximum

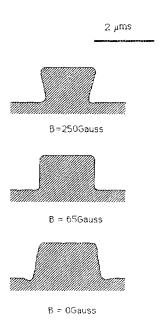


FIG. 7. Etch profiles of SiO_2 for various magnetic field strengths at 3 mTorr CF₄ and 0.45 W/cm² as taken from SEM photographs. The specimens were exposed to the processing plasma until 1.5 μ m of SiO_2 was etched away.

appears to be a result of the maximum number of ions bombarding the Si surface with at least the critical threshold energy as described above. The maximum C/F ratio could be a result of the accumulated excess carbon residue on the surface caused by the increased etch rate. It is likely that the reduced polymer layer is partly responsible for the low selectivity of SiO_2 over Si obtained in CF_4 plasmas when the etch rate was a maximum.

Etch profiles of SiO_2 observed by SEM are shown schematically in Fig. 7 for the same conditions as Fig. 2. The change in the etch profiles obtained when changing magnetic field strength, when correlated with the dc self-bias voltage, shows that an ion energy of $\sim 100~\rm eV$ is sufficient to yield a vertical feature. At low magnetic field strengths, tapered side etching and trenching was predominant due to degradation of the mask by direct sputtering. However, at high magnetic fields, where the ion energies arriving at the wafer were very small and the radicals and ions in the plasma were plentiful, a reentrant profile was obtained. This profile could be caused by a deviation of the incident ion trajectories to more grazing angles due to the high magnetic field strength. ¹⁸

V. CONCLUDING REMARKS

Cylindrical magnetron reactive ion etching in rf discharges has been studied as a function of magnetic field strength. We found that increasing the magnetic field strength generates a higher density of ions and radicals, and therefore potentially increases the etch rate. The increasing B field, though, decreases the dc self-bias voltage and hence the energy of the activating ion flux. These opposing effects yield an optimum applied magnetic field with respect to etching rates of Si and SiO₂ in CF₄ and CF₄/H₂ plasmas. The rate limiting step, though, is the need for a minimum dc self-bias voltage, and hence incident ion energy to activate the surface etching process. The optimum etch rate occurs near 60 G for moderate power deposition (0.45 W/cm²), a combination which also yields vertical wall features.

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¹J. A. Thornton and A. S. Penfold, in *Thin Film Processes*, edited by J. L. Vossen and W. Kern (Academic, New York, 1978), p. 75.

²R. K. Waits, in Ref. 1, p. 131.

³Y. Horiike, H. Okano, T. Yamazaki, and H. Horie, Jpn. J. Appl. Phys. 20, L817 (1981).

⁴D. C. Hinson, I. Lin, W. H. Class, and S. Hurwitt, Semicond. Int. 6, 103 (1983).

⁵K. Hirobe and H. Azuma, J. Electrochem. Soc. **132**, 938 (1985).

⁶G. Y. Yeom, J. A. Thornton, and M. J. Kushner, J. Appl. Phys. (to be published).

⁷T. H. Yuzuriha, W. E. Mlynko, and D. W. Hess, J. Vac. Sci. Technol. A 3, 2135 (1985).

⁸J. T. C. Yeh, K. R. Grebe, and M. J. Paimer, J. Vac. Sci. Technol. A 2, 1292 (1984).

⁹I. Lin, D. C. Hinson, W. H. Class, and R. L. Sandstrom, Appl. Phys. Lett.

- 44, 185 (1984).
- ¹⁰I. Lin, D. Hinson, W. Class, and R. Sandstrom, Electrochem. Soc. Extended Abstracts 83-1, 254 (1983).
- ¹¹R. J. Contolini and L. A. D'Asaro, J. Vac. Sci. Technol. B 4, 706 (1986).
- ¹²A. A. Bright, S. Kaushik, and G. S. Oehrlein, in *Plasma Processing and Synthesis of Materials*, edited by D. Apelian and J. Szekely (Materials Research Society, Pittsburgh, 1987), p. 217.
- ¹³T. E. Wicker and T. D. Mantei, J. Appl. Phys. **57**, 1638 (1985).
- ¹⁴M. F. Leahy and G. Kaganowicz, Solid State Technol. 30, 99 (1987).
- ¹⁵G. Y. Yeom, J. A. Thornton, and A. S. Penfold, J. Vac. Sci. Technol. 6, 3156 (1988).
- ¹⁶J. W. Coburn and M. Chen, J. Appl. Phys. 51, 3134 (1980).
- ¹⁷R. d'Agostino, F. Cramarossa, S. De Benedictis, and G. Ferraro, J. Appl. Phys. 52, 1259 (1981).
- ¹⁸The angular distribution of ions arriving at the surface after passing through a magnetized rf sheath has been studied using a particle simulation. Unpublished data provided by J. Caughman.