

Selective reactive ion etching of tungsten films in CHF₃ and other fluorinated gases

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The use of reactive ion etching (RIE) with fluorinated gas plasmas, such as SF₆, CF₄, CBrF₃, and CHF₃ mixed with oxygen, to achieve selective patterning of tungsten films is reported. The etch rates of W, Si, and SiO₂ were measured as a function of oxygen percentage in fluorinated gas plasmas under various conditions. Experiments on selectivity indicate that a CHF₃/70%O₂ mixture under 20 sccm, 200 W, 20 mTorr etching conditions results in W:Si and W:SiO₂ etch rate ratios of 1.6:1 and 1.8:1, respectively. Optimized W:Si and W:SiO₂ selectivity ratios 4:1 and 4.8:1 have been obtained at 60 mTorr/150 W and 260 mTorr/200 W plasma conditions. For reverse selectivity, the optimum W:SiO₂ etch rate ratio measured is 1:4.6 in pure CHF₃ gas. The optimum W:Si reverse selectivity of 1:11.6 is obtained with an SF₆/5%O₂ mixture plasma. A vertical-to-lateral etch ratio of 4:1 was measured with CHF₃/70%O₂, 200 W, 10 mTorr, 20 sccm. The etching mechanisms of tungsten due to chemical and physical processes in various fluorocarbon gases under the RIE mode have been investigated and the role of etching species such as fluorine, bromine, and oxygen is discussed.

I. INTRODUCTION

Refractory metals such as W or Mo are being increasingly used in (VLSI) circuits for contact vias, gate, and interconnect materials due to their high conductivity and high melting point.¹⁻³ Recently, there has been considerable interest in W metallization because of its selective deposition properties.²⁻⁵ Since interconnections need to be deposited and patterned over various underlying materials with a minimum disturbance of the existing structure, we have investigated sputter-deposited W films, annealed by rapid thermal processing and patterned by reactive ion etching. The sputtering technique has the advantages of being essentially substrate-independent, taking place at room temperature and being able to cover large areas fairly easily. The rapid thermal annealing (RTA) technique,^{6,7} with its very short operating time and high power density, was used to reduce the W resistivity and improve the quality of W thin film while preventing such effects as oxidation of the W film, and dopant redistribution.⁷ Reactive ion etching was chosen because of the need for anisotropic fine line patterning.

The main objective of this work, therefore, is to investigate the conditions under which the patterning of W films could be performed selectively with respect to Si and SiO₂. Since there are occasions during the fabrication process where the reverse selectivity is also highly desirable, in other words, a W etch rate which is lower than that of other materials present, especially SiO₂ and Si, this was investigated as well. The fluorinated gases, SF₆/O₂,⁸⁻¹⁰ CF₄/O₂,⁹ and CBrF₃/O₂¹¹ known to etch W films either have not previously been investigated in the low-pressure reactive ion etching (RIE) mode necessary for fine-line patterning or have not exhibited the necessary selectivity.

II. EXPERIMENTAL CONDITIONS

Tungsten films were deposited at room temperature by dc magnetron sputtering from a 99.97% purity W target in an

Ar plasma. A W sputtering rate of 10 nm/min was generally used. After deposition, W films were treated by RTA (AG Assoc. HeatPulse 120/T) using a broadband, high-intensity tungsten lamp in Ar ambient atmosphere from 500 to 1100 °C for a duration of 10–90 s. The purity of the argon gas used for both deposition and annealing was higher than 99.999%.

The etching experiments were carried out in a parallel plate reactor (Plasma Therm PK1241, 13.65 MHz) equipped with a computer-controlled grating monochromator for measuring optical emission within the plasma. The fluorinated gases used in our investigation were SF₆ (99.997% purity), CF₄ (99.9%), CBrF₃ (> 99%), and CHF₃ (> 98%) mixed with O₂ (99.99%). Emission spectra from the plasma, in the wavelength range between 200 and 800 nm, were monitored during etching through a quartz window located on the sidewall of the chamber. The concentrations of plasma species which are the reactants during etching are not necessarily linearly proportional to their emission intensities. Noble gas Ar or N₂^{12,13} actinometry has been used to determine the excitation efficiency of the plasma in promoting species from the ground state to the excited state responsible for the optical emissions. Thus one can obtain the relation between measured emission intensity and actual concentration in the plasma. In this work, the Ar actinometry technique is used and the relative concentrations of plasma species, such as F, O, H, and Br, are deduced from their emission intensities in different fluorinated gas mixtures.^{14,15} During experiments, a small amount of Ar gas, 0.6 sccm (3%), is added to the constant total flow rate of 20 sccm. A linearly increasing Ar (750 nm) emission intensity with increasing Ar flow rate (concentration) is observed, in agreement with previous results. The addition of the Ar gas to the feed gas does not alter the emission intensity of the other species present in plasma under different etching gases and conditions. Therefore, all data presented in this work have been calibrated to their relative concentrations simply

by dividing their emission intensity by Ar emission intensity.

To provide a suitable basis of comparison, the rf power, pressure, and gas flow rate were generally kept constant at 200 W (0.42 W/cm^2), 20 mTorr, and 20 sccm, respectively. To determine the etch rate in various gas plasmas, aluminum was used as a thin-film mask since it is suitable for both low- and high-percentage oxygen mixtures in the plasma. The Al mask was subsequently removed by wet etching for step height determination by a profilometer (Dektak). The anisotropy of the etching process was investigated by scanning electron microscopy (Nanometrics Cwickscan II).

III. RESULTS

Tungsten films of 300–500 nm were deposited on Si and SiO_2 for annealing and etching experiments. RTA was found to be very effective at reducing the resistivity of the W films by changing annealing time and temperature. The lowest resistivity value of $13 \mu\Omega \text{ cm}$ was obtained for 1100 °C, 60 s anneal in Ar ambient. X-ray diffraction patterns of W thin films deposited on oxidized Si(100) wafers were taken for each annealing temperature and compared to the as-deposited films. It was found that with increasing temperature the W films became strongly [110] oriented. In the etching experiments reported here, all W films were deposited and annealed as described above.

The reactive ion etching rates were determined as a function of oxygen percentage in CF_4 , SF_6 , CBrF_3 , and CHF_3 . In Fig. 1(a), the W etch rate for CF_4 plasma, along with the etch rates of Si and SiO_2 , is shown as a function of oxygen

percentage (from 0% to 90%) at a power of 200 W, a pressure of 20 mTorr, and a total flow rate of 20 sccm. In Fig. 1(b) is shown the corresponding dc self-bias and the plasma density of fluorine [F] and oxygen [O] based on optical emission intensity at 703.7 and 780 nm, respectively. The addition of relatively small amounts of oxygen to CF_4 increases the Si etch rate as the oxygen consumes fluorocarbon radicals and liberates additional fluorine species.¹⁶ Beyond a certain concentration, however, increasing amounts of oxygen have the opposite effect, as the oxygen-rich mixture dilutes the CF_4 gas and also lowers the energy of electrons in the plasma, which in turn reduces the electron-induced dissociation rate of CF_4 . Another effect important at high O_2 concentrations is the competition for active etching sites on the surface between [F] and chemisorbed O atoms.¹⁶ In general, however, the variation of the [F] density with $\text{O}_2\%$ is roughly mirrored in the Si etch rate.

The W etch rate behavior with $\text{O}_2\%$ in the CF_4 plasma appears to follow the [F] density, but the relationship is much less pronounced. However, all three parameters (Si and W etch rates, [F] density) exhibit a peak value for a 20% oxygen mixture. In our reactive ion etching (RIE)-mode experiments, the shift of maximum etch rate from maximum [F] concentration is reduced by the presence of a fairly high self-bias voltage ($> 400 \text{ V}$) which produces more energetic ions, capable of removing some of the chemisorbed oxygen or oxyfluorides from the surface. At high- O_2 concentrations, tungsten oxyfluorides can form in the plasma. The oxyfluorides are less volatile than tungsten hexafluoride and can retard the etching process through the formation of a surface oxyfluoride layer.¹⁷ Indeed, Picard and Turban have reported¹⁰ that W etching in CF_4/O_2 plasma at high pressure generates substantial ionized tungsten oxyfluorides. For the CF_4/O_2 RIE process, the W:Si etch rate selectivity is considerably less than unity for O_2 mixtures of $< 50\%$. For O_2 mixtures $> 50\%$, the selectivity does increase above unity (for example, 2:1 at 80% O_2), but under the restriction of rather low etch rates (40 and 20 nm/min for W and Si, respectively, at 80% O_2).

The etch rates of W, Si, and SiO_2 in SF_6/O_2 mixtures are shown in Fig. 2(a). The corresponding dc self-bias and the relative density of fluorine and oxygen in the plasma are shown in Fig. 2(b). The greater abundance of fluorine species in SF_6/O_2 mixtures results in a much greater Si etch rate. The maximum Si etch rate of $2.2 \mu\text{m}/\text{min}$ occurs at 10% O_2 concentration, even though the peak [F] density takes place for 30% O_2 . This result is very similar to that reported by Pinto *et al.*¹⁸ for Si RIE at 10 mTorr, 50 sccm, and 0.4 W/cm^2 , namely a peak etch rate of $1.3 \mu\text{m}/\text{min}$ at 10% O_2 . The offset between the maximum Si etch rate and the peak [F] density present in SF_6 etching versus its absence in CF_4 plasma can be explained by the considerably lower (\sim a factor of 2) dc bias found in the former case at small oxygen percentages, which is probably less effective in removing chemisorbed oxygen from the surface. Indeed, Pinto *et al.*¹⁸ report that as the power density (and consequently the dc bias) is lowered the resulting etch rate is not only lowered, but the peak in the etch rate versus O_2 shifts to lower oxygen concentrations. The maximum etch rate of 180

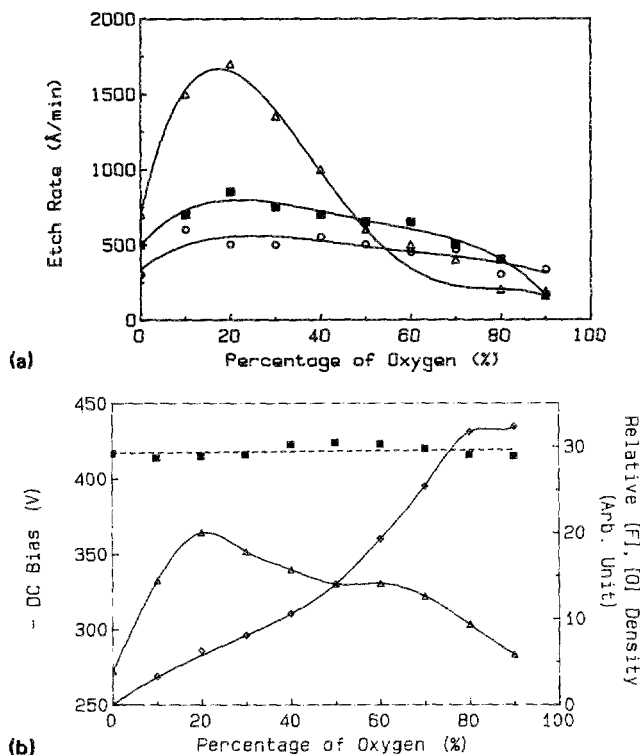


FIG. 1. (a) Etch rate of \blacksquare :W, \triangle :Si, and \circ : SiO_2 vs percentage of O_2 in CF_4 and O_2 plasma, at 200 W, 20 sccm, 20 mTorr, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle : [F], \diamond : [O] atomic density vs percentage of oxygen.

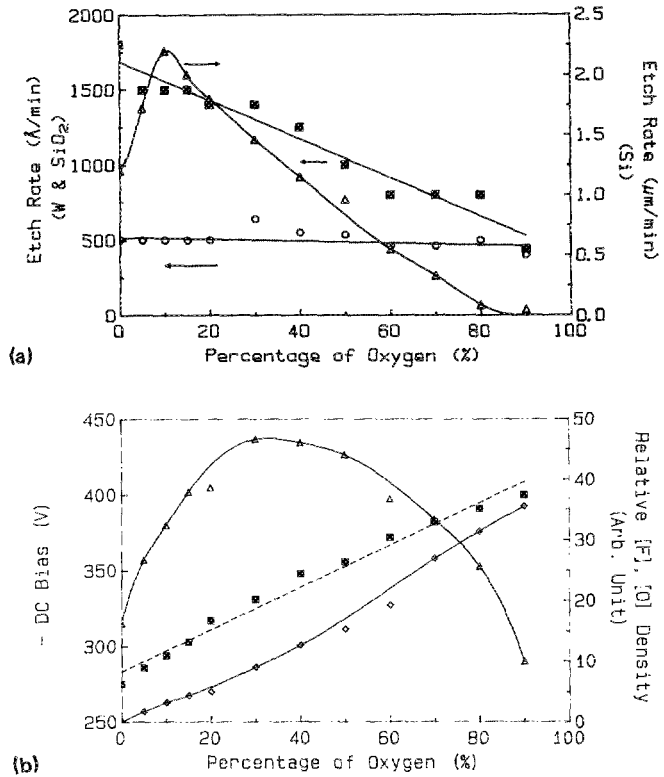


FIG. 2. (a) Etch rate of \blacksquare :W, \triangle :Si and \circ :SiO₂ vs percentage of O₂ in SF₆ and O₂ plasma, at 200 W, 20 sccm, 20 mTorr, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle :[F], \diamond :[O] atomic density vs percentage of oxygen.

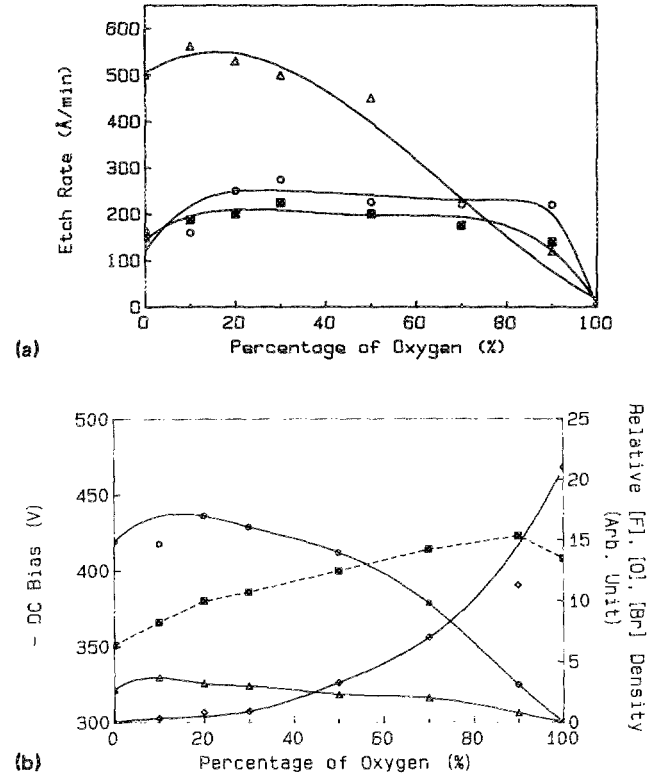


FIG. 3. (a) Etch rate of \blacksquare :W, \triangle :Si, and \circ :SiO₂ vs percentage of O₂ in CBrF₃ and O₂ plasma, at 200 W, 20 sccm, 20 mTorr, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle :[F], \diamond :[O], \circ :[Br] atomic density vs percentage of oxygen.

nm/min occurs for pure SF₆ gas and the etch rate decreases as O₂ increases, which is similar to the results reported by Randall and Wolfe.⁸

In CBrF₃ and O₂ mixtures, the maximum etch rate of Si occurs at 10% O₂, which coincides with the maximum [F] peak. The maximum etch rate for W is much lower than that achieved in nonbromine-containing fluorinated gases. One possible explanation for the low-etch rate in CBrF₃ lies in the properties of the tungsten hexafluoride. The W bromides and chlorides have much higher melting and boiling points than the fluoride.¹⁹ It is therefore, very likely that the W bromides have a vapor pressure similar to the W chlorides, which in turn are known to have a much lower vapor pressure than WF₆.¹⁷ Further, the tungsten oxybromide also has higher melting and boiling points than the oxyfluoride. Therefore, it is reasonable to explain the lower CBrF₃ etch rate as being due to the formation of less volatile compounds. The dc bias and density of [F], [O], and [Br] (at 336 nm) measured during W etching in CBrF₃ are shown in Fig. 3(b). The selectivity of W to Si has a maximum of only 1.2:1 at 90% O₂, since it is restricted by very low etch rates for W (14 nm/min) and Si (12 nm/min). In the work of Schattenburg *et al.*,¹¹ lower pressure (10 mTorr) was shown to improve the etching profile, but it is unlikely to improve the selectivity. Finally, data for pure O₂ RIE, shown in Fig. 3(a), indicate that almost no etching takes place for all materials investigated in the absence of the halogen gas.

The reactive ion etching rates using CHF₃ and O₂ mixtures are shown in Fig. 4(a) and the corresponding dc bias,

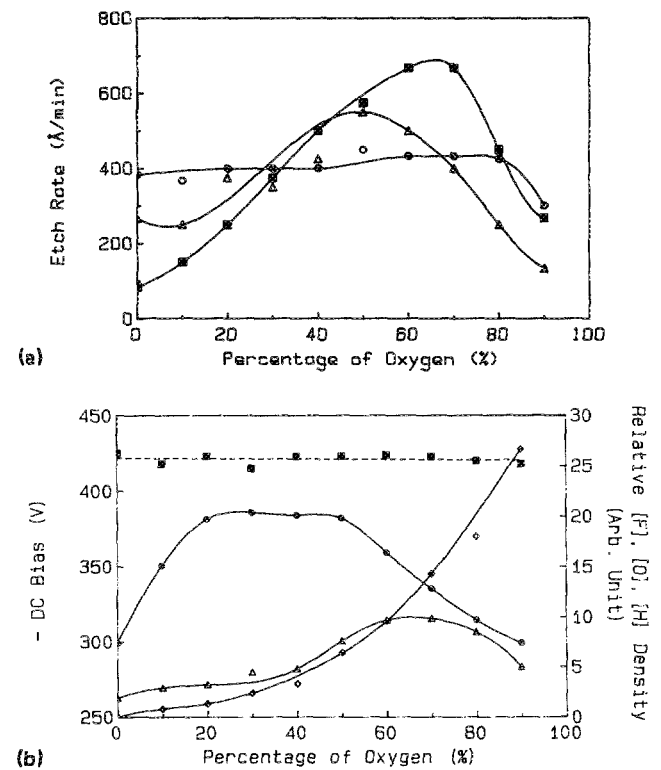


FIG. 4. (a) Etch rate of \blacksquare :W, \triangle :Si and \circ :SiO₂ vs percentage of O₂ in CHF₃ and O₂ plasma, at 200 W, 20 sccm, 20 mTorr, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle :[F], \diamond :[O], \circ :[H] atomic density vs percentage of oxygen.

[F], [O], and [H] density (based on emission at 486 nm) are shown in Fig. 4(b). In the pure CHF_3 plasma, the fluorine species concentration is diluted because of the high-hydrogen concentration and by direct reaction with H forming HF molecules.²⁰ This decrease in [F] reduces the Si etch rate considerably, while the presence of HF increases the SiO_2 etch rate.²¹ In Fig. 4(b), we show that addition of large amounts of O_2 does result in a slight increase in the [F], with a peak at $\sim 65\%$ O_2 . The Si etch rate peaks at 50% O_2 with a value of 55 nm/min. By comparison, the maximum Si etch rate in SF_6 is 2.2 $\mu\text{m}/\text{min}$ or 40 times larger.

The W film etch rate in CHF_3/O_2 plasma is also strongly affected by the lower [F] concentration, especially at low $\text{O}_2\%$ levels, where the [H] concentration is quite high. However, in the vicinity of the [F] peak at 60%–70% O_2 mixtures, the W etch rate increases substantially. The highest W etch rate was 66.7 nm/min at 70% O_2 and the corresponding etch rate ratios for W to Si and SiO_2 are 1.6 and 1.8. For reverse selectivity, the optimum etching takes place in pure CHF_3 , where the following etch rate ratios are obtained: W to Si and SiO_2 of 1:3.2 and 1:4.6.

To optimize the W-to-Si etching selectivity, the pressure in the reactor chamber has been varied from 20 to 260 mTorr for $\text{CHF}_3/70\%$ O_2 , 20 sccm, 200 W plasma conditions. The resulting pressure dependence of the etch rates are shown in Fig. 5(a). Error bars are used to indicate the range of measurements at each pressure. Initially, the W etch rate increases rapidly with pressure, from 67 nm/min at 20 mTorr to 170 nm/min at 88 mTorr. At pressures higher than 100 mTorr, the W etch rate exhibits substantial saturation. The

Si etch rate increases monotonically with pressure, while the SiO_2 etch rate has a broad maximum at around 100 mTorr pressure. The optimum W-to-Si selectivity of 3.6:1 and 4.8:1 for W: SiO_2 are measured at 88 mTorr and 260 mTorr respectively. The corresponding dc bias and [F], [O], and [H] concentrations are shown as a function of pressure in Fig. 5(b). As expected, the dc bias decreases monotonically with increasing pressure due to increasing number of collisions within the plasma. The corresponding lower plasma electron energy reduces the efficiency of the dissociation process. On the other hand, increasing the pressure increases the molecular density of the gas. Therefore, the net effect of these two factors determines the pressure dependence of the various species in the plasma. The oxygen concentration is seen to increase rapidly with pressures up to 60 mTorr, followed by a much more gradual rise at higher pressure. The fluorine concentration also increases with pressure, up to 110 mTorr and thereafter maintains a constant value. Finally, the hydrogen density follows a nonmonotonic behavior with a peak occurring at 60 mTorr. While the Si etch rate appears to closely follow the [F] concentration, the W etch rate has a more complicated dependence, combining the effects of both [F] and [O].

The effect of varying rf power on the etch rate is shown in Fig. 6(a). The power is varied from 100 to 300 W at 70% O_2 , 20 sccm, 60 mTorr. The W, Si, and SiO_2 etch rates exhibit a monotonically increasing dependence on plasma power. At an rf power of 150 W, the W etch rate is 120 nm/min and the etching selectivity of W to Si is 4.0:1. The optimum selectivity of W to SiO_2 is 3.9:1 at 150 W. In Fig. 6(b) the dc bias is shown to increase linearly with rf power. However, both the

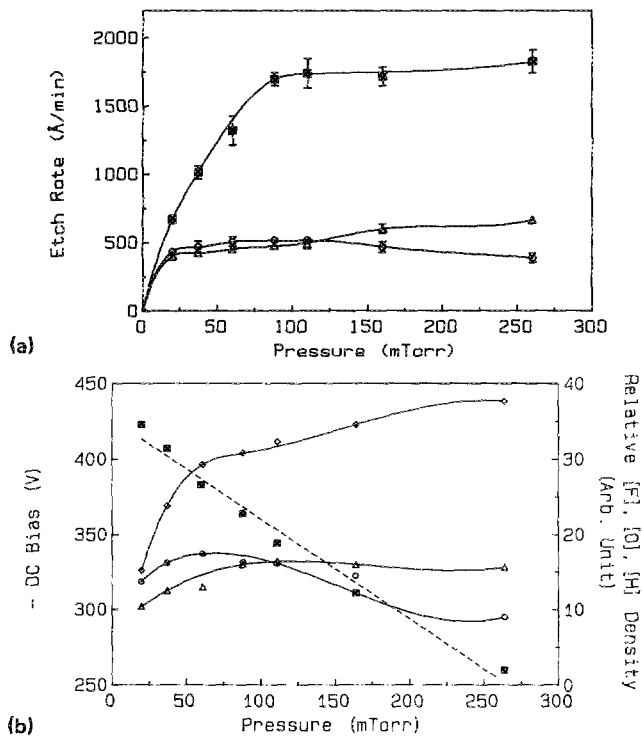


FIG. 5. (a) Etch rate of \blacksquare :W, \triangle :Si and \circ : SiO_2 vs pressure in 30% $\text{CHF}_3/70\%$ O_2 plasma, at 200 W, 20 sccm, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle : [F], \diamond : [O], \circ : [H] atomic density vs pressure.

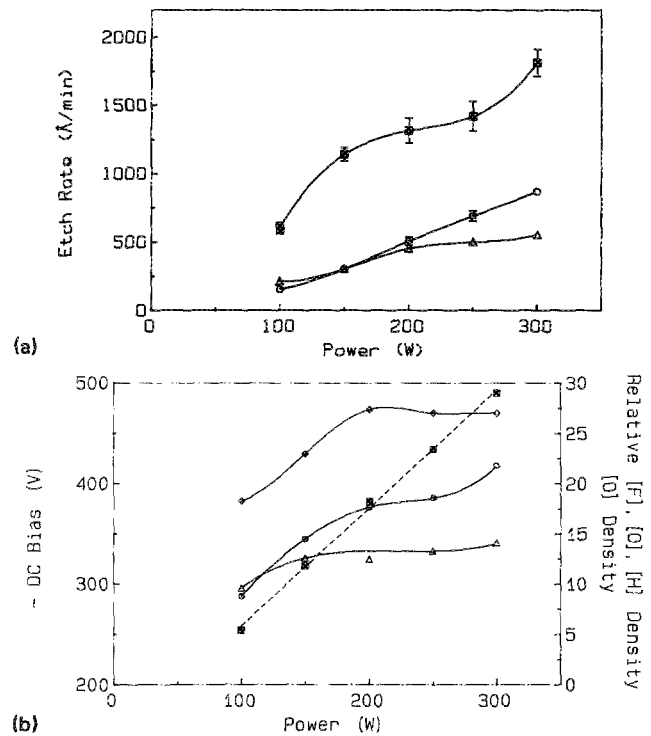


FIG. 6. (a) Etch rate of \blacksquare :W, \triangle :Si and \circ : SiO_2 vs power in CHF_3 and 70% O_2 plasma, at 20 sccm, 60 mTorr, RIE mode. (b) \blacksquare :dc self-bias and relative \triangle : [F], \diamond : [O], \circ : [H] atomic density vs power.

[F] and [O] concentrations saturate beyond a certain power level. It is, therefore, likely that at high power levels physical mechanisms dominate the etching process by removing low-volatility products, such as WOF_x , which can form on the surface under high-percentage oxygen conditions.¹⁰

The optimum selectivities of reactive ion etching are summarized in Table I. A W:Si etch rate ratio greater than unity was shown for the first time to be achievable using $CHF_3/70\% O_2$, 200 W, 20 mTorr where a selectivity of 1.6:1 was measured. The selectivity can be increased to 4.0:1 by adjusting the plasma pressure and power. The highest reverse W:Si selectivity of 1:1.6 was obtained with $SF_6/5\% O_2$, 200 W, 20 mTorr. For W:SiO₂ selectivity, the optimum value of 4.8:1 was obtained at $CHF_3/70\%$, 200 W, 260 mTorr, while the optimum reverse selectivity is found in pure CHF_3 plasma.

The edge profile of W films etched by reactive ion etching was preliminarily investigated for conditions observed to produce optimum W-to-Si and W-to-SiO₂ selectivity. W films, 0.53 μm thick, were etched mainly in $CHF_3/70\% O_2$ gases. A 5- μm -W line on Si patterned with $CHF_3/70\% O_2$, (at 20 sccm, 200 W, and 20 mTorr) is shown in Fig. 7(a) with the Al mask layer still in place. A 0.22 μm undercut of the W film was measured when the etching is stopped at the Si substrate. The vertical-to-lateral etch ratio of the W film shown in Fig. 7(a) is 2.3:1. The etching directionality disappeared [Fig. 7(b)] when the pressure is increased to 60 mTorr. However, a vertical-to-lateral etch ratio of 4:1 is measured when the pressure is reduced to 10 mTorr, as shown in Fig. 7(c). This is due to the fact that the chemical reaction component of the W etch rate is reduced by the decreasing amount of reactive species at lower pressure, while the physical component is enhanced by the increasing self-induced dc bias.

IV. DISCUSSION

In this work, we have used fluorinated gases diluted with oxygen in a plasma reactor operating in the RIE mode at a generally fixed pressure, flow rate, and power. As discussed in the previous section, a very strong, but complex, relationship is evident between the amount of oxygen in each of the four fluorinated gases (CF_4 , SF_6 , $CBrF_3$, and CHF_3), the fluorine concentration and the resulting W and Si etch rates. In Table II we compare the effect of oxygen on our results

TABLE I. Maximum direct and reverse selectivities observed for W:Si and W:SiO₂.^a

| Selectivity | $CHF_3/70\%O_2$ | $CHF_3, SF_6/10\%O_2$ | $CBrF_3/10\%O_2$ |
|--------------------|---------------------|-----------------------|------------------|
| W:Si | 1.6:1 | 1:3.2 | 1:15 |
| W:SiO ₂ | 1.8:1 | 1:4.6 | 3:1 |
| W:Si | 88 mT ^b | 3.6:1 | ... |
| | 150 W ^c | 4.0:1 | ... |
| W:SiO ₂ | 260 mT ^b | 4.8:1 | ... |
| | 150 W ^c | 3.9:1 | ... |

^a RIE etching conditions: 200 W, 20 sccm, 20 mTorr.

^b RIE, 20 sccm, 200 W.

^c RIE, 20 sccm, 60 mTorr.

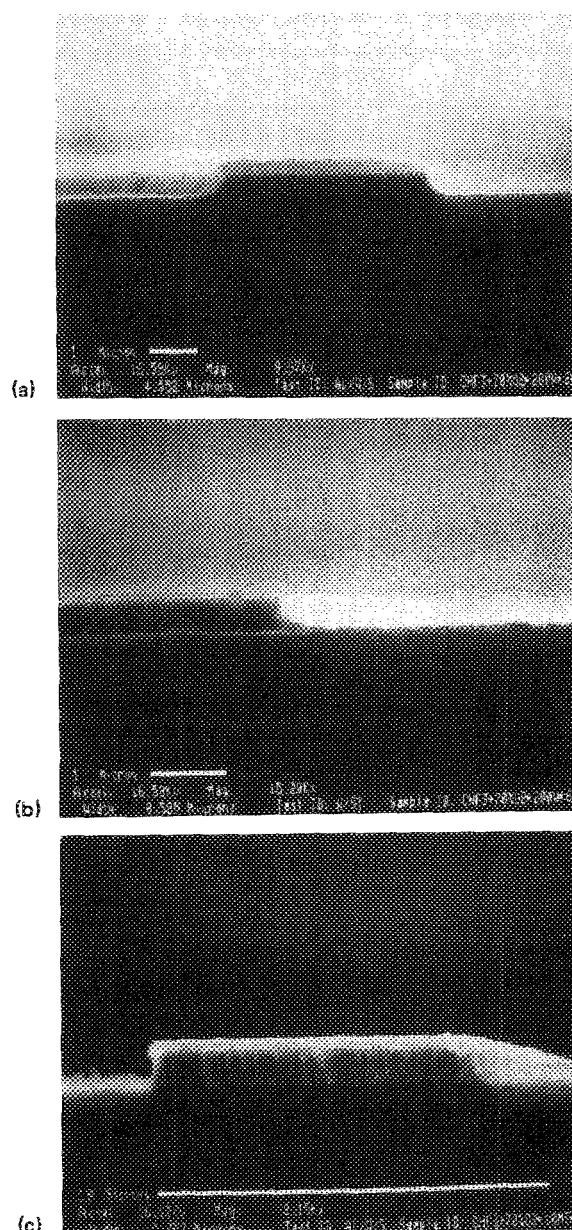


FIG. 7. (a) SEM picture of edge profile of 0.525 μm W film which was etched in $CHF_3/70\% O_2$, at 200 W, 20 sccm, 20 mTorr. An Al mask was used and various films were deposited on Si substrate as indicated. (b) SEM picture of edge profile of W on Si which was etched in $CHF_3/70\% O_2$, at 200 W, 20 sccm, 60 mTorr. (c) SEM picture of edge profile of W on Si which was etched in $CHF_3/70\% O_2$, at 20 sccm, 200 W, 10 mTorr (with Al mask).

with those of related work from the literature by indicating the O_2 percentage in the gas mixture at which the [F] density, and Si or W etch rates reach their maximum value. For comparison purposes, we have also included corresponding plasma etching results from the literature.

In the case of CF_4/O_2 mixtures, both our results with W RIE and those of others for W and Si plasma etching^{9,10} indicate a [F] peak at 20%–23% O_2 mixtures. However, under our RIE conditions the W and Si etch rate maximum are coincident with the [F] peak, whereas the PE results published indicate a shift in the maximum etch rate to lower

TABLE II. Comparison of results for fluorine/oxygen-based plasma-assisted etching of Si and W.

| Gases | CF ₄ /O ₂ | SF ₆ /O ₂ | CHF ₃ /O ₂ | CBrF ₃ /O ₂ | | |
|-----------------------------------|---|--|---|---|---|------------------|
| Mode, pressure, and power density | PE 350 mTorr 0.16 W/cm ² ^a and PE 200 mTorr 0.2 W/cm ² ^b | PE 200 mTorr 0.2 W/cm ² ^b PE 1 Torr ~1.8 W/cm ² ^d | RIE 20 mTorr 0.42 W/cm ² ^c | RIE 20 mTorr 0.42 W/cm ² ^c | RIE 20 mTorr 0.42 W/cm ² ^c | |
| [F] peak ^h | 20% ^a 20% ^b | 20% ^c | 30% ^b 30% ^d | 30% ^e | 65% ^e | 20% ^c |
| Si E.R. ^g peak | 12% ^a | 20% ^c | 30% ^d | 10% ^e 10% ^e | 50% ^e | 10% ^c |
| W E.R. ^g peak | 10% ^b | 20% ^c | 0% ^b | 0% ^e 0% ^f | 65% ^e | 30% ^c |

^aMogab *et al.* (Ref. 16).^bTang&Hess (Ref. 9) (W as-deposited at 350 °C).^cPan&Steckl (this work) (W RT annealed at 1110 °C).^dd'Agostino&Flamm (Ref. 22).^ePinto *et al.* (Ref. 18).^fRandall&Wolfe (Ref. 8) (W as-deposited at 25 °C).^gE. R. peak: Oxygen percentage for maximum etch rate.^h[F] peak: Oxygen percentage for maximum fluorine density.

oxygen percentage (10%–15%). In the case of SF₆/O₂ etching, both W PE and RIE of W and Si exhibit this shift. For CBrF₃/O₂ etching, the shift is found only for W. Finally, in the case of CHF₃/O₂, a shift is observed for Si RIE but not for W etching.

To understand the role of fluorine radicals in the reactive ion etching process we plot in Figs. 8, 9, and 10 the etch rates of Si, W, and SiO₂ as a function of measured fluorine density obtained at various oxygen mixtures. As can be seen, most

cases, with SiO₂ being a major exception, exhibit a substantial hysteresis effect, where for the same [F] concentration two widely different etch rates can result. This effect has been previously observed in the plasma etching of Si in CF₄/O₂¹⁶ and SF₆/O₂²² mixtures. As mentioned in Sec. III, this effect has been attributed¹⁶ to the competition between fluorine and oxygen atoms for chemisorption sites on the Si surface. Thus, the availability of increasing amounts of [F] does not necessarily result in an increasing etch rate, if it is

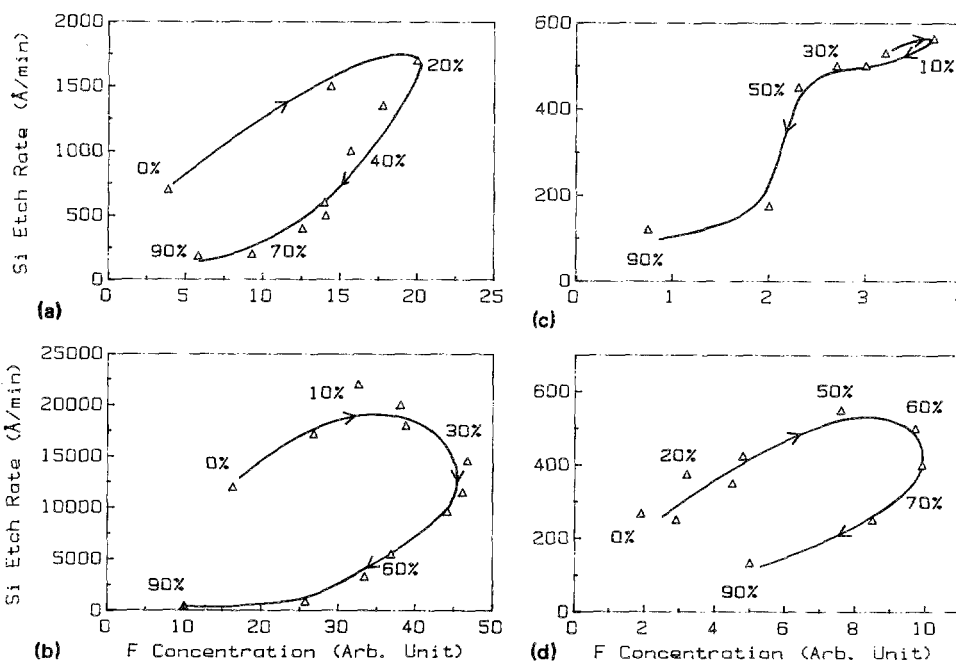


FIG. 8. Etch rate of Si vs [F] density in (a) CF₄, (b) SF₆, (c) CBrF₃, and (d) CHF₃ with O₂ plasma under RIE mode.

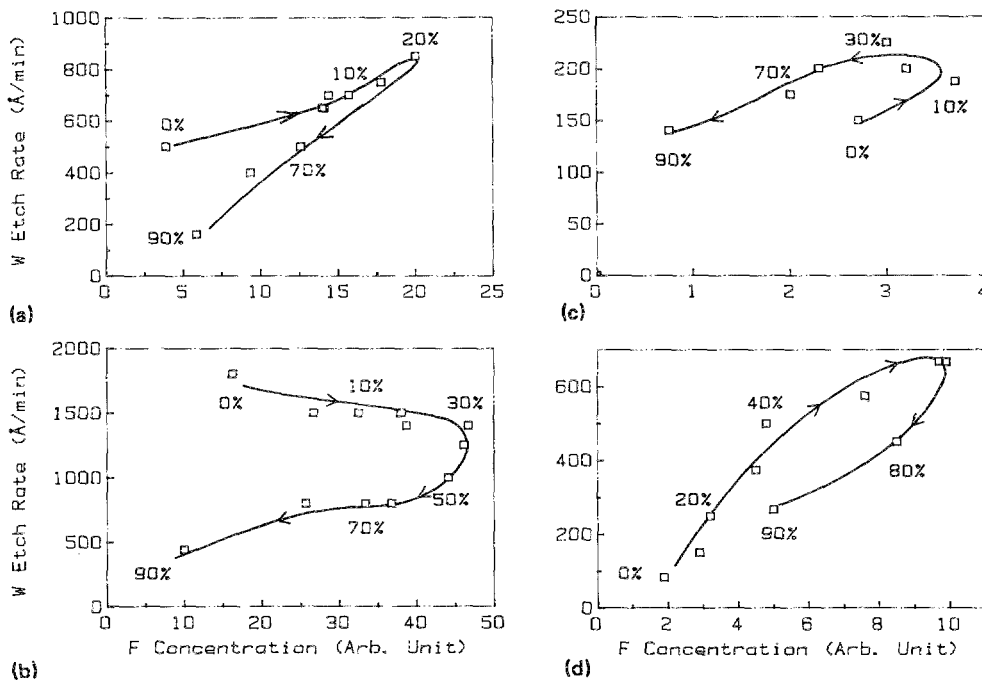


FIG. 9. Etch rate of W film vs [F] density in (a) CF₄, (b) SF₆, (c) CBrF₃, and (d) CHF₃ with O₂ plasma under RIE mode.

accompanied by an equal or greater increase in oxygen concentration. In the case of W RIE, our data also exhibit hysteresis, indicating that a similar mechanism is at work. The situation is quite different for SiO₂, since oxygen forms an intrinsic part of the material to be etched. Consequently, no hysteresis effect is observed, but rather a generally increasing trend in etch rate with [F], with a similarly large scatter in the data as reported by Mogab *et al.*¹⁶ for SiO₂ plasma etching in CF₄/O₂ mixtures.

To further elucidate the competing roles of fluorine and oxygen we have plotted in Fig. 11 the self-normalized Si and W etch rates as a function of the ratio of [F] to [O] concentrations in all four gas mixtures. The [O] intensity level at

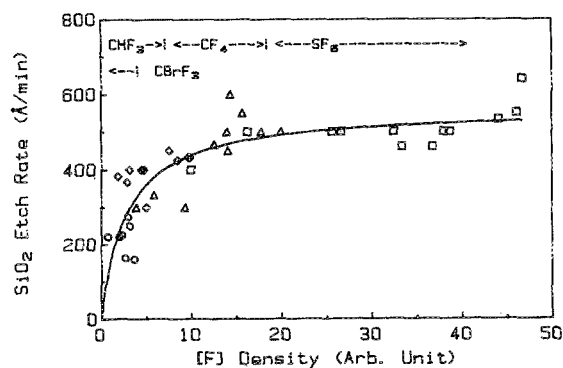


FIG. 10. Etch rate of SiO₂ vs [F] density in Δ :CF₄, \square :SF₆, \circ :CBrF₃, and \diamond :CHF₃ with O₂ plasma under RIE mode.

each point is taken with respect to the base line level found in the "pure" gas plasma. The arrows along each curve indicate the direction of increasing O₂% in each gases. The vertical arrows indicate the [F]/[O] ratio value for which the maximum [F] concentration is present. A number of comments can be made about the information contained in Fig. 11. First, the hysteresis effect in the etch rate is removed by taking both [F] and [O] into account. Second, the etch rate trends for Si and W are the same in each gas plasma. Third, the pattern is substantively different for RIE in CF₄/O₂, SF₆/O₂, and CBrF₃ from RIE in CHF₃/O₂. For the former, the etch rate increases with [F]/[O] ratio until it gradually reaches saturation followed, in some cases, by a minor decline. However, in the CHF₃/O₂ case, the pattern is clearly nonmonotonic with a pronounced peak in etch rate present at a [F]/[O] ratio of 1.2 for Si and ~ 0.85 for W. The decrease in etch rate after the peak takes place in mixtures with increasing levels of hydrogen. This clearly points out the inhibiting role of hydrogen on the W and Si etch rate.

V. SUMMARY

In summary, the reactive ion etching of W films, along with Si and SiO₂, was investigated in CF₄/O₂, SF₆/O₂, CBrF₃/O₂, and CHF₃/O₂ plasmas. A W:Si etch rate ratio greater than unity was for the first time obtained, in oxygen-rich CHF₃ mixtures. The variation of pressure and power was explored to optimize the etching selectivity and to improve sidewall etching profile. The competing roles of fluorine and oxygen in the etching process was investigated.

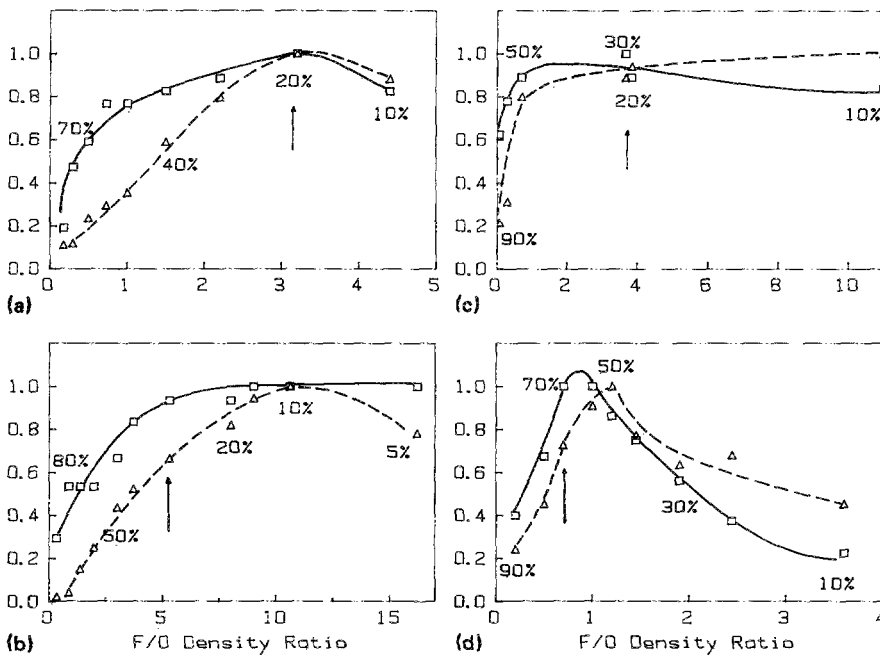


FIG. 11. The normalized etch rate ratio of ■:W and △:Si vs $[F]/[O]$ density ratio in (a) CF_4/O_2 , (b) SF_6/O_2 , (c) $CBrF_3/O_2$, (d) CHF_3/O_2 plasma.

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