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MATERIALS AND INTERFACES

Photoresist Trimming in Oxygen-Based High-Density Plasmas: Effect of HBr and Cl_2 Addition to CF_4/O_2 Mixtures

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The effects of HBr or Cl_2 addition to CF_4/O_2 plasmas on resist trimming were examined. Because the reactivity of halogens on trimming decreases from F to Br and then to Cl, the addition of HBr and Cl_2 to CF_4/O_2 decreases the trim rate. In contrast, the etch selectivity of the resist to the underlying polysilicon and the trim-rate uniformity are generally improved with the addition of enough HBr to CF_4/O_2, whereas addition of Cl_2 has the opposite effect in that it degrades the selectivity and uniformity. The constituents of the resist sidewall in different plasma etchants with HBr or Cl_2 gas added to CF_4/O_2 were examined using angle-resolved XPS to study how the trim rate is influenced by the sidewall films formed during resist trimming. The XPS results showed that the films formed on the resist sidewall had different constituents and concentrations according to the plasma chemistry. $CO_xBr_yF_z$ and $CO_xCl_yF_z$ films were formed on the resist sidewall during trimming with $HBr/CF_4/O_2$ and $Cl_2/CF_4/O_2$, respectively. The presence of halogen in the plasma affects the availability of the oxygen atom to the resist surface. A greater atomic concentration ratio of oxygen to carbon and a higher degree of halogenation of the films coincide with a higher trim rate.

I. Introduction

As the feature sizes of integrated circuits continue to shrink at a rate faster than the semiconductor road map, researchers have evaluated new strategies to make gate transistors smaller than the resolution allowed by the lithographic tools available for manufacturing. One such strategy is to decrease the feature dimension of the photoresist employed later as the etch mask, before the subsequent gate etching processes. This technique has also been proposed also because of the resolution limit of optical lithography. At present, it would be impossible using conventional lithography techniques alone to fabricate sub-0.1-μm gate electrodes because of the resolution limit of the current 248-nm lithography and immaturity of the 193-nm lithography process.[1,2] By using resist trimming techniques, controlled definition of deep-submicron features is permitted. The technique has been successfully employed to fabricate metal-oxide-semiconductor field-effect transistors (MOSFETs) with effective channel lengths as small as 40 nm using DUV lithography.[3] Similar techniques to reduce the line width of the masking materials have also been described as photoresist ashing,[3,4] oxide lateral etching,[5] or resist thinning[3,6,7] processes. All of these processes have the advantage of reducing the gate length without increasing the complexity of the lithography requirements.

The resist trimming process is applicable to all lithograph generation. The photoresist ashing technique has been applied to the fabrication of 0.15-μm MOSFET devices using the conventional g-line (436-nm) lithography approach of Chung et al.[4] With DUV lithography, Lee et al.[7] trimmed the photoresist prior to etching of an inorganic hardmask to pattern a polysilicon gate of 60 nm. Cunge et al.[8] have also reported using resist trimming for the fabrication of sub-50-nm gate electrodes. Researchers have also started to investigate the possibility of trimming using 193-nm lithography, but problems arise in that the new type of resist used collapses after trimming.[9] Studies have shown that resist trimming is both reproducible and uniform. Thus, it should be a viable technique for deep-submicron device manufacturing.[4−6,10]

For feasible applications in the semiconductor industry, vertical profiles, reasonable rates, and high selectivities with respect to the underlayer must be achieved simultaneously during resist trimming. In general, oxygen plasmas give higher rates of removal of the organic resist and higher etching selectivities than polysilicon and oxides. In most cases, a vertical profile is obtained by adding a second constituent that is known for the formation of passivating layers, such as a halogen-containing gas, to protect the sidewalls.[11,12] It

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has been reported that N_2, He, CHF_3,[13] Cl_2,[14,15] HBr,[14,16] and SO_2[17,18] gases are effective for the dry etching of resists.

The performance of resist trimming with HBr/O_2, Cl_2/O_2, and CF_4/O_2 has been evaluated previously.[19] Trimming in CF_4/O_2 exhibits the highest trim rate, followed by HBr/O_2 and then Cl_2/O_2 at the same percentage of halogen-containing gas in the mixture. In contrast, the resist-to-polysilicon selectivity is best in HBr/O_2 plasma and worst in CF_4/O_2 plasma. However, all three plasmas exhibit monotonically decreasing resist/polysilicon selectivities as a function of halogen gas percentage. Increasing the halogen gas flow increases the trim-rate nonuniformity because of the poorer halogen-containing plasma uniformity except for HBr, for which the nonuniformity is maintained fairly constant at all percentages of HBr gas. Also, no distortion of the resist profiles occurs for all three gas mixtures. Resist trimming with CF_4/O_2 has been shown to be reproducible and easily adaptable to the existing polysilicon gate etching process.[20] Sub-0.1-μm polysilicon lines with vertical sidewall profiles were fabricated successfully by trimming 120-nm-wide photoresists with CF_4/O_2 using conventional 248-nm lithography. As a continuation of our previous studies,[19,20] this paper examines the effect on resist trimming of the addition of a second halide gas, HBr or Cl_2, to the CF_4/O_2 plasma. An understanding of the effects of various halogens on trimming is useful for process optimization. The effects of the different ratios of the additive gas, HBr or Cl_2, to the main etchant, CF_4/O_2, on the changes in the trim characteristics, such as the trim rate and the selectivity to the polysilicon, as well as on the vertical profiles, and XPS chemical analyses of the resist sidewalls are reported in this article.

II. Experiments

The high-density and low-pressure plasma used for resist trimming was generated by an inductively coupled plasma (ICP) source (TCP9400DFM, Lam Research) excited using a 13.56 MHz RF power supply. The wafer was biased with an additional 13.56 MHz RF power source. For an ICP system, the plasma density and ion energy can be independently controlled by adjusting the RF source power and the RF bias voltage. The theory and characteristics of ICP plasma sources have been described by Keller et al.[21] To provide good thermal conductance between the wafer and the susceptor, wafer clamping and helium backside cooling were used. In this study, all trimming and etching were carried out at 70 °C. Reactant gases were introduced into the etcher from the center of the chamber. The gas flow rate and chamber pressure can be controlled independently by adjusting the mass flow rate controller and throttle valve. The operating conditions used in this study were as follows: source power, 250 W; bias voltage, −50 V; pressure, 10 mTorr; total gas flow rate, 130 sccm. These conditions correspond to the optimized process developed for trimming in CF_4/O_2 for the fabrication of sub-0.1-μm transistors using 248-nm lithography.[22]

In this study, patterned 200-mm wafers masked with chemically amplified photoresist (CAR) were used. The gate stack consisted of a very thin gate oxide and a 200-nm layer of doped polysilicon. Bottom antireflective coating (BARC) (60 nm) and chemically amplified resist film (425 nm) were subsequently spin-coated onto the polysilicon film. Conventional 248-nm optical lithography was used to pattern the resist lines to 0.12 μm. Resist trimming was then performed using the oxygen-based halogen mixture plasmas in the aforementioned commercial ICP etcher. With the trimmed resist as an etch mask, etching of the polysilicon was executed in the same ICP etcher using HBr/Cl_2 plasma.

The test structures used in this study consisted of alternate photoresist lines and spaces arrays. Polysilicon lines with spacing-to-line width ratios on each side greater than 5 are referred to as isolated lines. The nested lines are commonly referred to as dense lines. In this work, the test structure before trimming had a spacing-to-line ratio near 2, i.e., 0.12 μm for line width and 0.25 μm for spacing. This is the design-rule structure used for test chip inspection, which also resulted from a compromise to minimize the microloading effect.[19]

The line width before trimming is often referred as the developed inspection critical dimension (DICD). The line width after trimming is called the final inspection critical dimension (FICD). All CD measurements were performed using an in-line Hitachi scanning electron microscope (SEM). The trim-rate nonuniformity, σ, was calculated over 13 points across the wafer. The trim rate was calculated by dividing the line width difference between the DICD and the FICD by the trimming time. The trim-rate nonuniformity was defined as the standard deviation of the trim rate relative to the mean value. Cross-sectional SEM was employed to examine the profile. Selectivity is identified as the ratio of the etch rate of the photoresist to the etch rate of the underlying polysilicon. Blanket-deposited resist wafer and polysilicon wafer were used to determine the selectivity. Likewise, the etch rate was calculated as the change in film thickness divided by the etch time. The thickness measurements before and after etching were performed using an optical probing system (Therma-Wave, Fremont, CA).

The XPS measurements were performed ex situ on an AXIS HSi spectrometer (Kratos Analytical Ltd., Manchester, U.K.) using a monochromatic Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The measurements were taken with the charge neutralizer on. The pressure in the analysis chamber was maintained at 5.0×10^{-8} Torr or lower during each measurement. The spectra of elements were curve-fitted (using the Kratos software VISION 2.0) with Gaussian peaks to determine the relative atomic concentration of various bonding. The adjustments required, following the energy shifts caused by charging of the photoresist surface, were made by using an internal reference provided by the C 1s core level of the hydrocarbon peak, the commonly accepted binding energy of which is 285.0 eV. XPS analysis was carried out in regions where the aforementioned line and space structure arrays were spread over an area in excess of the ca. 400×400 μm^2 X-ray beam spot. Therefore, the photoelectrons detected by the analyzer represent contributions from many line and space features. The sidewall film analysis was performed using the approach described by Oehrlein et al.[23] The angle between the X-ray source and electron analyzer was fixed at 45°. An angle of 90° between the sample surface and the electron analyzer was used to analyze the tops of the features and the bottoms of the spaces. The sample was tilted to 60° with respect to the axis of the electron analyzer when the analyses of the tops and

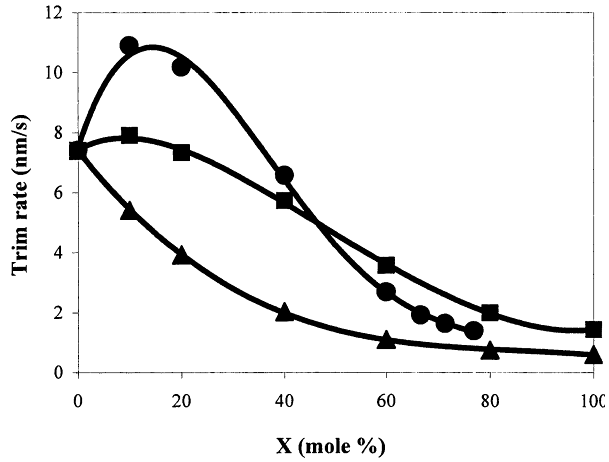


Figure 1. Effect of HBr (■) or Cl_2 (▲) addition to CF_4/O_2 (●) on the trim rate. Equal amounts of HBr or Cl_2 and CF_4 are added to the CF_4/O_2 mixture. The total gas flow rate is kept the same at all time. *X* stands for the total molar percentage of the halogen gases in the gas mixtures. *X* represents CF_4 for CF_4/O_2 (●), HBr + CF_4 for $HBr/CF_4/O_2$ (■), and Cl_2 + CF_4 for $Cl_2/CF_4/O_2$ (▲).

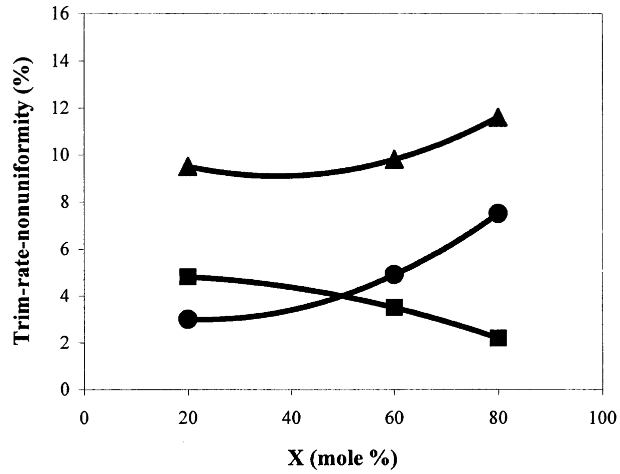


Figure 2. Changes in the trim-rate nonuniformity when equal amounts of halogen HBr (■) or Cl_2 (▲) and CF_4 were added to the CF_4/O_2 (●) plasma. The total gas flow rate was kept the same at all times. *X* denotes the total molar percentage of the halogen gases in the gas mixtures. *X* represents CF_4 for CF_4/O_2 (●), HBr + CF_4 for $HBr/CF_4/O_2$ (■), and Cl_2 + CF_4 for $Cl_2/CF_4/O_2$ (▲).

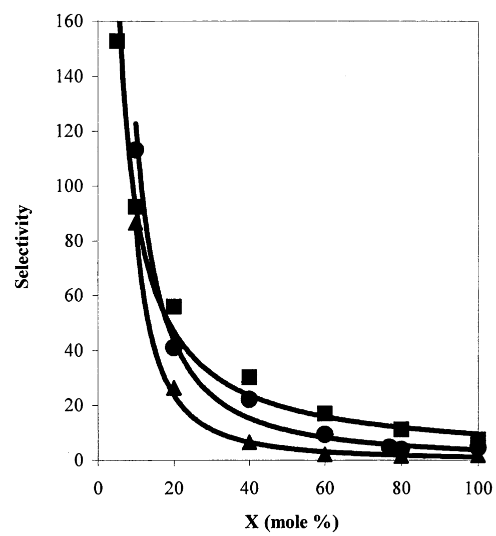


Figure 3. Effect of HBr (■) or Cl_2 (▲) addition to CF_4/O_2 (●) on the selectivity of the resist to the polysilicon. Equal amounts of HBr or Cl_2 and CF_4 were added to the CF_4/O_2 mixture. The total gas flow rate was kept the same at all times. *X* represents the total molar percentage of the halogen gases in the gas mixtures. *X* represents CF_4 for CF_4/O_2 (●), HBr + CF_4 for $HBr/CF_4/O_2$ (■), and Cl_2 + CF_4 for $Cl_2/CF_4/O_2$ (▲).

sidewalls of the features were done. The sample was tilted so that the trench bottom would not be irradiated by the incident flux of X-rays because of the intervening resist mask/polysilicon features and, therefore, no X-ray-induced photoelectron emission from the trench bottom would occur.

III. Results

Using resist trimming with CF_4/O_2 plasma as the reference,[19] the effect of adding another halogen-containing gas, HBr or Cl_2, on resist trimming was evaluated. The second halogen-containing gas was added to the CF_4/O_2 mixture in two proportions: either in the same amount as CF_4 at varying CF_4/O_2 ratio or in varying ratios to CF_4 at constant CF_4/O_2 ratio. The effects of adding HBr or Cl_2 to CF_4/O_2 on the trim characteristics, such as the trim rate, trim-rate nonuniformity, selectivity, and passivation layer on the photoresist sidewall, were studied by comparison with the results of using HBr/O_2, Cl_2/O_2, or CF_4/O_2.[20]

A. Trimming with the Same Amount of HBr or Cl_2 as CF_4 Added to CF_4/O_2 for Constant Total Gas Flow. 1. Trim Rate and Trim-Rate Nonuniformity. Figure 1 shows the change in trim rate when equal amounts of additive gas and CF_4 were added to the CF_4/O_2 gas mixture. The total gas flow was maintained at 130 sccm. The trim rate obtained using CF_4/O_2 only is incorporated in the figure as a reference.[19] The addition of Cl_2 to the CF_4/O_2 gas mixture caused the trim rate to drop. With increasing Cl_2 and CF_4 in the $Cl_2/CF_4/O_2$ mixture, the trim rate decreased dramatically and monotonically. When trimming with $HBr/CF_4/O_2$, the trim rate increased slightly with the addition of small amounts of HBr and CF_4 and then decreased gradually with increasing halides percentage. There was a synergistic effect between CF_4 and HBr at an overall HBr and CF_4 percentage greater than ca. 50% in that the trim rate became even higher than that obtained by using CF_4/O_2 mixtures only (Figure 1).

Figure 2 shows the change in the trim-rate nonuniformity when HBr or Cl_2 was added. When equal amounts of HBr and CF_4 were added, the trim-rate nonuniformity decreased with increasing halide amount. However, the trim-rate nonuniformity increased greatly with increasing Cl_2 addition to the CF_4/O_2 mixtures.

2. Selectivity. The selectivity is commonly defined as the ratio of the etch rate of the photoresist to that of the underlying polysilicon. High resist/polysilicon selectivity is desired such that no etching of the underlying polysilicon would take place when it was exposed to the trimming chemistry for some period of time toward the end of the resist etch process. Figure 3 shows that the addition of equal amounts of Cl_2 and CF_4 in CF_4/O_2 plasmas makes the selectivity become worse at higher overall percentages of halogen gas in the mixtures, whereas the addition of enough HBr to CF_4/O_2 mixture improves the selectivity to polysilicon. The selectivity decreases with increasing halides percentage. Very high selectivity (>70) can be obtained for halide contents of less than 10% in both $HBr/CF_4/O_2$ and $Cl_2/CF_4/O_2$ plasmas. At total molar percentages of halogens

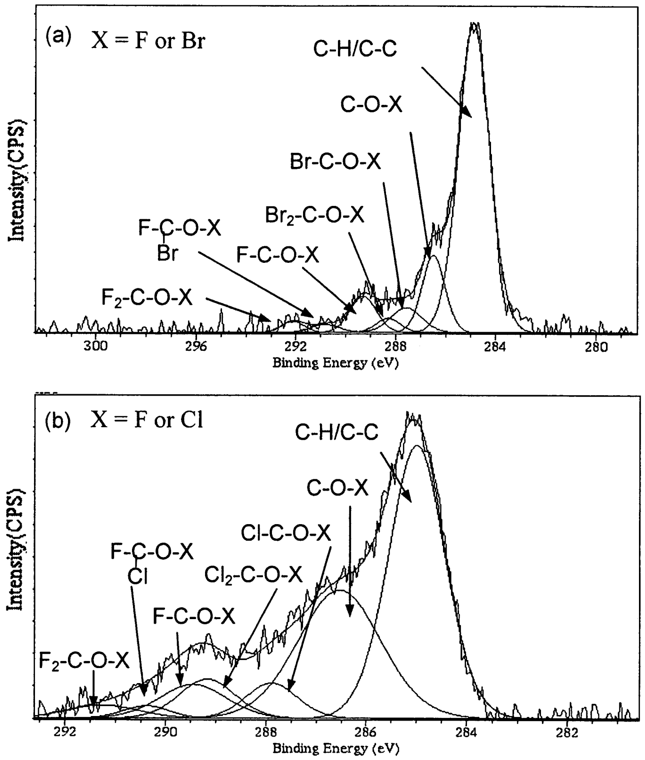
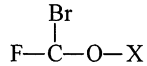


Figure 4. C 1s XPS spectra of resist sidewall obtained at glancing angle for three different plasma chemistries: (a) HBr/CF_4/O_2 (X = F or Br), (b) Cl_2/CF_4/O_2 (X = F or Cl). The peak at 285.0 eV is due to the bulk photoresist.

greater than ca. 20%, the HBr/CF_4/O_2 chemistry gives the largest selectivity. That is, the addition of HBr in this case can improve the selectivity of the photoresist over the underlying polysilicon.

3. XPS Resist Sidewall Analysis. The quantitative coverages of carbon, oxygen, and halogen were derived from spectra recorded with the charge neutralizer turned on. The adjustments required because of the energy shifts caused by charging of the photoresist surface were made by using an internal reference provided by the C 1s level of the hydrocarbon peak, the commonly accepted binding energy of which is 285.0 eV.

The halogens F, Cl, and Br have quite different electronegativities and induce shifts of C 1s core level to higher binding energies. For example, the primary shift of C 1s caused by F, i.e., C−F bond, is 2.9 eV, whereas those caused by Cl and Br, i.e., C−X (X = Cl or Br), are 1.5 and 1 eV, respectively.[24] Even the secondary substitution effects by the halogens on the neighboring carbon atoms are still significant. They are 0.7, 0.3, and <0.2 eV, respectively, for F, Cl, and Br.[24] Likewise, the oxygen induces shifts of the C 1s core level to a higher binding energy by 1.5 eV per C−O bond.[24] Nonetheless, the secondary effect of the X in the C−O−X bond on C 1s is insignificant (only $\pm$0.4 eV).[24] Hence, the C−O−F and C−O−Cl bonds, as well as the C−O−F and C−O−Br bonds, are grouped together as "C-O-X" in Figure 4, because they are practically indistinguishable. In contrast, the peaks representing the F−C−O−X, Br−C−O−X, Br_2−C−O−X, F_2−C−O-X, and



have to be separated, as they are easily discernible.

Table 1. Atomic Concentrations on the Resist Sidewall after Trimming with HBr/CF_4/O_2 or Cl_2/CF_4/O_2[a]

	atomic concentration (%)			
	Br 3d	F 1s	O 1s	C 1s
HBr/CF_4/O_2	0.59	4.27	55.63	39.50
	Cl 2p	F 1s	O 1s	C 1s
Cl_2/CF_4/O_2	7.23	12.92	38.72	41.13

[a] Equal amounts of HBr or Cl_2 and CF_4; molar ratio of the halides to O_2 maintained at 3.3:1.

Table 1 shows the elemental concentration on the resist sidewall after trimming with HBr/CF_4/O_2 and Cl_2/CF_4/O_2 at a halide/oxygen molar ratio of 3.3 and equal amounts of HBr or Cl_2 and CF_4 in the mixture. The analysis indicates that $CO_xBr_yF_z$ or $CO_xCl_yF_z$ is formed. Although the amount of halogen-containing gases added is the same in each mixture, the halogen atomic concentration on the sidewall varies. The amount of halogen found on the resist sidewall decreases as the atomic weight of the halogen increases.

The XPS analysis was carried out on the resist processed with the gas mixtures having equal amounts of HBr or Cl_2 and CF_4 and a halide-to-O_2 molar ratio of 3.3. The atomic ratios were determined from the total peak areas. It should be mentioned that the atomic concentrations of these species are in proportion to the areas of the XPS peaks normalized by the corresponding sensitivity factors, not the peak areas themselves. However, in this case, the sensitivity factors for C 1s in these various bonds can be regarded as the same, in practice. Thus, the XPS peak areas could be used directly as an indicator of the atomic concentrations of these species.

The oxygen-to-carbon elemental (O/C) ratio for HBr/CF_4/O_2 is 1.12, that for Cl_2/CF_4/O_2 is 0.43, and thatfor CF_4/O_2 is 0.79. The addition of HBr to CF_4/O_2 plasma increases the O/C elemental ratio, whereas the addition of Cl_2 to CF_4/O_2 decreases the ratio. As seen from Figure 1, the trim rate in HBr/CF_4/O_2 is higher than that in CF_4/O_2, whereas the trim rate in Cl_2/CF_4/O_2 is lower. The change in the O/C ratio is consistent with the change in the trim rate. Hence, it is proposed that the trim rate is affected by the availability of oxygen to carbon, i.e., the oxygen-to-carbon atomic ratio. Indeed, neutral oxygen radicals act as etchants for polymers by cleaving the polymer chains into smaller segments. As oxygen is the dominant trimming species,[19] an increase in the amount of oxygen per carbon atom will increase the trim rate accordingly.

Figure 4 shows the C 1s spectra recorded on the resist sidewall after trimming in HBr/CF_4/O_2 and Cl_2/CF_4/O_2. After the carbon spectra were deconvoluted and curve-fitted using a Gaussian peak shape, the bondings could be categorized as C−C/C−H, C−O−X, X−C−O−X, and X_2−C−O−X (X = halogen). The intensities of the different carbon bonding components for each gas mixture are listed in Table 2.

Because the XPS analysis of the blanket photoresist before photoresist trimming process indicated no halogen signal, the carbon−halogen XPS signal must arise from the CO_yX_z polymer deposited on the resist sidewall during the trimming. Using the peaks arising from a carbon atom with at least one halogen bond, the relative occurrence of X_y−C−O−X (y = 1 or 2) to C−O-X was calculated. A higher relative amount of X_y−C−O−X bonds means that the carbon becomes more haloge-

Table 2. Percent Atomic Compositions of the Photoresist after Being Trimmed by the Different Plasmas[a]

	composition (at. %)			
	C−C/C−H	C−O−X	X−C−O−X	X_2−C−O−X
$HBr/CF_4/O_2$[b]	69.22	12.39	11.78	6.61
$Cl_2/CF4/O_2$[c]	45.32	31.45	12.19	11.04
CF_4/O_2[d]	54.26	18.54	19.16	8.04

[a] C 1s Gaussian fitting used to decompose spectra. [b] X = F or Br. [c] X = F or Cl. [d] X = F.

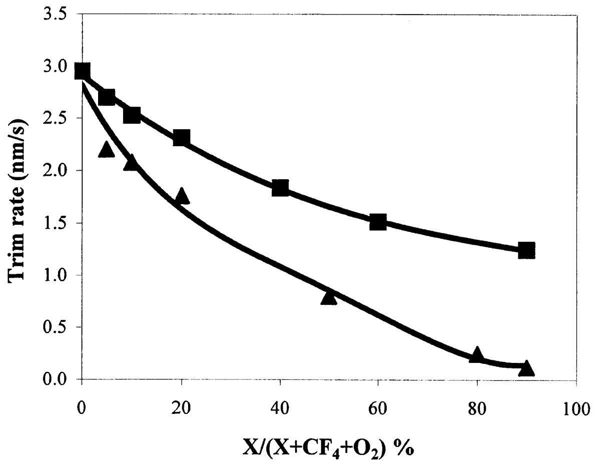


Figure 5. Dependence of trim rate on HBr (■) or Cl_2 (▲) percentage in the three-component gas mixture having CF_4/O_2 = 3:2 (by moles). *X* represents HBr for $HBr/CF_4/O_2$ (■) and Cl_2 for $Cl_2/CF_4/O_2$ (▲). The total gas flow rate is always maintained at 130 sccm.

nated. The F_y−C−O−F to C−O−F ratio in CF_4/O_2 plasma is 1.47. Table 2 shows that the degree of halogenation (i.e., the ratio of X_y−C−O−X to C−O-X) of the passivation film on the resist sidewall increases slightly to 1.48 with the addition of HBr to CF_4/O_2 and decreases to 0.73 with the addition of Cl_2. Data in the previous section demonstrate that the resist trim rate decreases in the order of trimming in $HBr/CF_4/O_2$, CF_4/O_2, and $Cl_2/CF_4/O_2$ for equal amounts of HBr or Cl_2 and CF_4 and a halide-to-O_2 molar ratio of 3.3. It is consistent that a higher trim rate takes place on a more halogenated carbon film.

B. Trimming with the Addition of HBr or Cl_2 to CF_4/O_2 with a Fixed CF_4-to-O_2 Ratio for Constant Total Gas Flow. 1. Trim Rate and Trim-Rate Nonuniformity. Figure 5 shows the change in trim rate when the percentage of HBr or Cl_2 in the three-component mixture is increased while the molar ratio of CF_4-to-O_2 and the total gas flow are maintained constant. The molar ratio of CF_4-to-O_2 is always set at 3:2, and the total gas flow is kept at 130 sccm. The trim rate curves decrease monotonically with increasing amount of HBr or Cl_2 relative to CF_4 in the CF_4/O_2 mixture. However, Cl_2 addition induces a greater drop in the trim rate than HBr addition. Figure 6 shows that the trim-rate nonuniformity decreases with increasing percentage of HBr in the $HBr/CF_4/O_2$ mixture, whereas the trim-rate nonuniformity increases with increasing addition of Cl_2 to the $Cl_2/CF_4/O_2$ mixture.

2. Selectivity. Figure 7 shows the change in resist/polysilicon selectivity with increasing amount of HBr or Cl_2 relative to CF_4 added to the CF_4/O_2 mixture. Without the addition of HBr or Cl_2, the selectivity of CF_4/O_2 at 60% CF_4 was about 7.5. With increasing addition of HBr to CF_4/O_2, the selectivity increased to

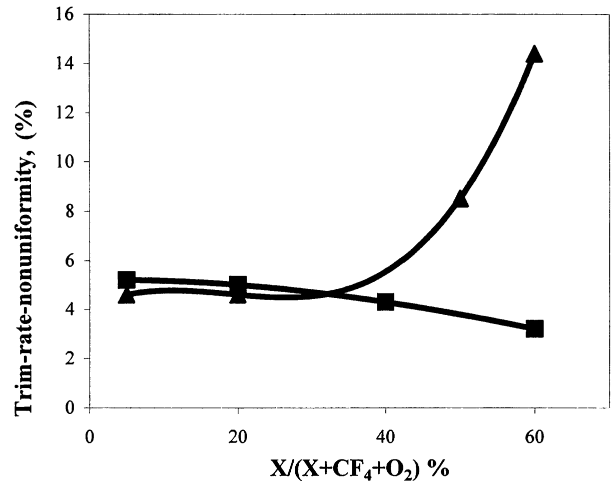


Figure 6. Changes in the trim-rate nonuniformity, σ, when an increasing amount of HBr (■) or Cl_2 (▲) relative to CF_4 and O_2 is added to the plasma. The molar ratio of CF_4 to O_2 is maintained at 3:2. *X* represents HBr for $HBr/CF_4/O_2$ (■) and Cl_2 for $Cl_2/CF_4/O_2$ (▲).

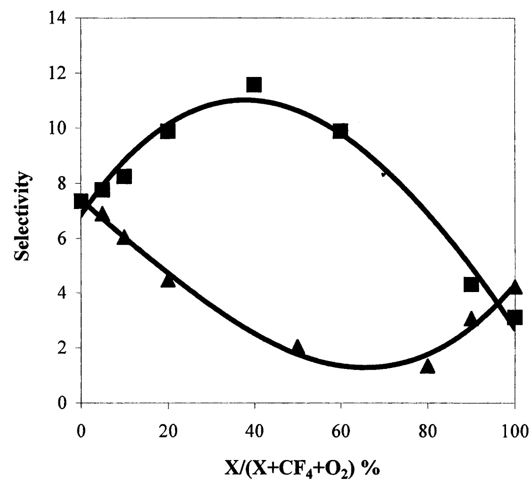


Figure 7. Dependence of the selectivity of the resist to polysilicon on the HBr (■) or Cl_2 (▲) percentage in the three-component gas mixture having a molar ratio of CF_4 to O_2 equal to 3:2. *X* represents HBr for $HBr/CF_4/O_2$ (■) and Cl_2 for $Cl_2/CF_4/O_2$ (▲).

a maximum of about 11 at 40% HBr (i.e., 40% HBr, 36% CF_4, and 24% O_2) and then decreased sharply. This is because the etch rate of the polysilicon drops to a minimum and then increases again. However, HBr improved the resist/polysilicon selectivity generally. Selectivity in the $Cl_2/CF_4/O_2$ plasma exhibited a trend opposite to that of the $HBr/CF_4/O_2$ plasma. With increasing addition of Cl_2 to CF_4/O_2, the selectivity decreased to a minimum of about 1.3 and then increased.

Figure 8 displays SEM micrographs of the resulting polysilicon gate in very small dimensions using the optimal conditions of the resist trimming in $HBr/CF_4/O_2$ and polysilicon etching in HBr/Cl_2. The critical dimensions are 63 and 54 nm, respectively, for the dense-line and the isolated-line patterns. Very good vertical profiles of the polysilicon gate were achieved in this resist trimming process.

IV. Discussion

In the oxidative decomposition reaction of a polymer, such as the photoresist used in this work, a C−H bond

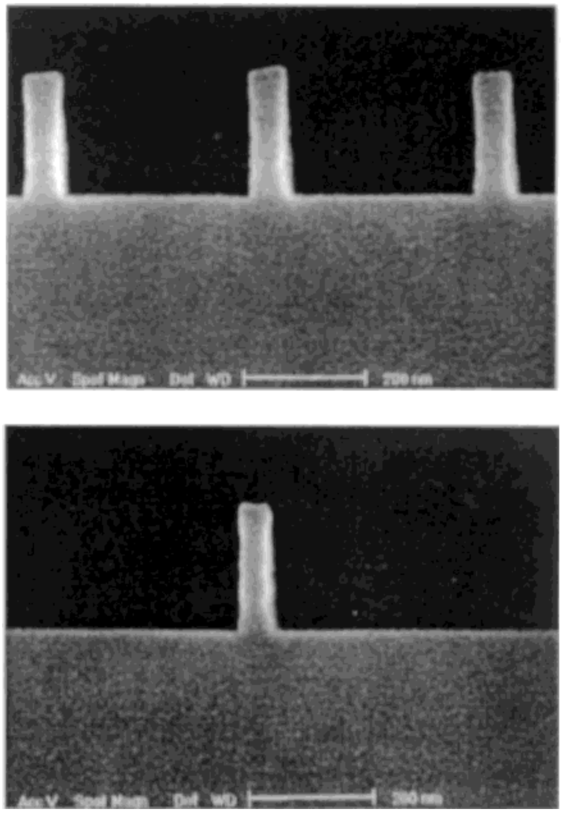


Figure 8. Polysilicon profile when the resist is trimmed with HBr/CF_4/O_2. The critical dimensions (CD) shown here are ca. 63 and 54 nm for dense and isolated lines, respectively.

is broken first to form a radical polymer species,[25] which then reacts with the oxygen molecule at this site to form a peroxide radical. Moreover, the halogen atoms can also enhance the fast abstraction of the hydrogen atoms from the resist surface and, subsequently, allow the peroxide to form by rapid reaction with oxygen radicals, which break the polymer chain into volatile fragments.[19,26]

For trimming performance in two-component oxygen/halogen gas mixtures,[20] trimming in CF_4/O_2 gives the highest trim rate, followed by in HBr/O_2, whereas trimming in Cl_2/O_2 gives the lowest rate. Because neutral oxygen radicals are polymer etchants, their availability will profoundly influence the trim rate of the photoresist.[19] Chlorine can scavenge the oxygen atom by forming stable halogen oxides[27] (i.e., $Cl + O \rightarrow ClO$), resulting in a decrease of reactive oxygen concentration in the plasma. Because of the relatively high bond strength of HBr compared to BrO, the removal of oxygen by the formation of BrO is unlikely. In contrast, a small amount of CF_4 addition can enhance the dissociation of O_2 in the plasma.[28] This shows that the reactivity of the halogen in resist trimming decreases from F to Br and then to Cl. Thus, it is suspected that the addition of HBr or Cl_2 to CF_4/O_2 will decrease the trim rate, as is certainly observed in the Figure 1.

It is noticed that the curves of the trim rate for the three-component mixtures containing oxygen and the two halogens in equal amounts is virtually the average of the trim-rate curves corresponding to the two-component plasmas having oxygen and the specific individual halogens. For example, the trim-rate curve of HBr/CF_4/O_2 with equal amounts of HBr and CF_4 (Figure 1) is very close to the average of the corresponding trim-rate curves for HBr/O_2 and CF_4/O_2. The addition of HBr, generally but not in all cases, decreases the trim rate. However, the trend of the trim rate implies that the effect of HBr is not very considerable. Although it is not easily observed in Figure 1, the addition of a small amount of HBr to CF_4/O_2 indeed raises the trim rate slightly. Nevertheless, the effect of Cl_2 is quite significant in decreasing the trim rate of CF_4/O_2. The trim-rate curve is being dragged down, decreasing monotonically. Figure 5 shows the change in trim rate with increasing amount of HBr and Cl_2 at a constant CF_4/O_2 ratio of 3:2 and a constant total gas flow. Again, it shows that the trim rate decreases with increasing addition of HBr and Cl_2 to CF_4/O_2. The addition of Cl_2 causes a more dramatic decrease in trim rate than HBr. As mentioned previously, CF_4, Cl_2, and HBr affect the oxygen radicals differently. The aforementioned additivity of the trim-rate curves implies that these halides in plasmas will still interact with oxygen radicals independently.

The additive effect between different halogens is also observed in the changes in the trim-rate nonuniformity and the selectivity when equal amounts of HBr or Cl_2 and CF_4 are added to the CF_4/O_2 mixture. Previous results show that trimming in HBr/O_2 has the best uniformity and Cl_2/O_2 has the worst among the three two-component mixtures investigated.[20] This suggests that the addition of HBr might improve the nonuniformity, whereas the addition of equal amounts of Cl_2 and CF_4 to the CF_4/O_2 mixtures will lead to a negative effect.

As seen in Figure 2, Cl_2 and CF_4 have a synergistic effect on the trim-rate nonuniformity. The trim-rate nonuniformity increases significantly with increasing addition of equal amounts of Cl_2 and CF_4 to the CF_4/O_2 mixtures. In contrast, the nonuniformity is improved with HBr addition. The effect of HBr overrides that of CF_4 in that the trim-rate nonuniformity decreases with increasing HBr and CF_4 percentage. The positive effect of HBr and the negative effect of Cl_2 on the trim rate uniformity are again demonstrated in Figure 6. The trim-rate nonuniformity increases significantly with increasing Cl_2 relative to CF_4, whereas the nonuniformity decreases with increasing HBr.

In addition, it is known that trimming in CF_4/O_2 has the worst selectivity and HBr/O_2 has the best among the three two-component gas mixtures studied.[20] This is because atomic fluorine, even in the absence of ion bombardment, reacts rapidly with the underlying polysilicon and the spontaneous etching of Si by Br is very slow.[29] Hence, the selectivity improves when equal amounts of HBr and CF_4 are added to CF_4/O_2 and degrades with the addition of Cl_2 to CF_4/O_2, as shown in Figure 3. The selectivity decreases with increasing halogen percentage, because the etch rate of the polysilicon increases and that of the resist decreases simultaneously. However, with an increasing amount of HBr relative to a fixed CF_4/O_2 ratio in the HBr/CF_4/O_2 mixture, the selectivity increases to a maximum and then decreases as shown in Figure 7. This is because the etch rate of the polysilicon decreases to a minimum and then increases significantly at a higher HBr concentration. Figure 7 also shows that the selectivity generally decreases with increasing amount of Cl_2 relative to CF_4 added to CF_4/O_2 plasma.

The atomic concentrations of the different components detected on the resist sidewall in HBr/CF_4/O_2 and Cl_2/CF_4/O_2 are reported in Table 1. The HBr or Cl_2 is added to the CF_4/O_2 plasma in the same amount as the CF_4 and at the CF_4-to-O_2 molar ratio of 3.3. The XPS analysis shows the formation of $CO_xBr_yF_z$ or $CO_xCl_yF_z$ on the resist sidewall, respectively. Coincidently, the amount of halogen atoms on the sidewall is related to the atomic weight of the halogen. Br, being the heaviest, is the least detected on the sidewall, whereas F, being the lightest, has a much higher concentration than the other halogens. As atomic oxygen is the dominant trimming species in the oxygen-based plasma mixtures,[12,30] the higher the amount of oxygen available to each carbon atom, the higher the trim rate. The addition of HBr or Cl_2 to CF_4/O_2 will affect the availability of the oxygen and, hence, the oxygen-to-carbon (O/C) ratio. The ratio increases when HBr is added but decreases when Cl is added to the CF_4/O_2 plasma. This is consistent with the results shown in Figure 1 in that the trim rate is higher with the addition of equal amounts of HBr and CF_4 at a 77% total halide concentration, whereas the trim rate is lower with Cl_2 addition at the same overall halogen concentration in the mixtures.

Our previous work in examining the trimming performance in HBr/O_2, CF_4/O_2, and Cl_2/O_2 shows that a higher trim rate is accompanied by a higher degree of fluorination of resist sidewall film.[20] In this study, the XPS analysis again shows that a more halogenated carbon film accompanies a higher trim rate. It was found that the trim rate gives the same trend as the increasing ratio of $X_y-C-O-X/C-O-X$. The degree of halogenation is the highest when trimming with $HBr/CF_4/O_2$, followed by CF_4/O_2 and then $Cl_2/CF_4/O_2$, which is also the decreasing order of trim rate at the same percentage of halogen.

This result is explained by the involvement of halogen in the trimming reaction. Halogen atoms can help the reaction by removing hydrogen atoms from the polymer and, hence, breaking the polymer chain.[26] The bond breakage is accelerated by an increasing degree of halogenation. Thus, a higher trim rate is accompanied by a higher degree of halogenation of the resist sidewall surface.

V. Conclusions

The characteristics of resist trimming were investigated in the case of CF_4/O_2-based gas chemistries with the addition of another halide: HBr or Cl_2. The addition of a second halide to CF_4/O_2 generally decreases the trim rate. It is demonstrated that a reasonable trim rate and a higher selectivity to the underlying polysilicon are achieved for $HBr/CF_4/O_2$ chemistry. The reason for the good selectivity to the underlying polysilicon is that the HBr is very inert toward polysilicon. Dry development of polysilicon using the trimmed resist as a mask was performed. Polysilicon gates in very small dimensions but with vertical profiles of the polysilicon were achieved under optimized conditions of resist trimming in $HBr/CF_4/O_2$ and polysilicon etching in HBr/Cl_2 (Figure 8). HBr also has the effect of improving the trim-rate uniformity. In contrast, the addition of Cl_2 to CF_4/O_2 decreases the trim rate significantly, trimming with $Cl_2/CF_4/O_2$ gives a lower selectivity to the underlying polysilicon and a poorer uniformity compared to CF_4/O_2. XPS analysis shows the formation of $CO_xBr_yF_z$ and $CO_xCl_yF_z$ on the resist sidewalls when trimming with $HBr/CF_4/O_2$ and $Cl_2/CF_4/O_2$, respectively. This analysis clarified that the fluorine is an important element for protection of the resist sidewall. Halogens affect the trim rate by changing the availability of oxygen to each carbon atom or the oxygen-to-carbon atomic ratio and the degree of halogenation of the sidewall film. A higher trim rate occurs when the oxygen-to-carbon elemental ratio and the halogenation degree of the sidewall film are higher.

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