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Poly(ferrocenyldimethylsilanes) for Reactive Ion Etch Barrier Applications

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The behavior of poly(ferrocenyldimethylsilane) (PFS) under reactive ion etching conditions was investigated. Due to the presence of iron and silicon in the main chain, the polymer was found to be relatively stable toward oxygen plasma etching compared to common organic polymers. Depending on the conditions employed, the etching rate ratio for poly(isoprene) vs poly(ferrocenyldimethylsilane) ranged from 20:1 to 50:1. During etching, a thin iron- and silicon-containing oxide layer was formed at the surface of the organometallic polymer. The oxide layer was characterized by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) using depth profiling. Iron was found to be more resistant toward removal by oxygen plasma compared to silicon. Iron in the polymer also makes it resistive to CF_4/O_2 etching. A regular pattern consisting of parallel lines of PFS on a solid substrate was obtained by micromolding in capillaries (MIMIC) (a microcontact printing technique), which could be transferred into the underlying substrate. Under the conditions employed, silicon and silicon nitride substrates were etched at approximately 20 nm/min, whereas no thickness decrease was observed for the poly(ferrocenyldimethylsilane) film, even after etching times exceeding 10 min.

Introduction

Production of integrated circuits is often performed using low-pressure radiofrequency plasmas to etch thin films.[1] The patterns of interest are formed by lithographic processes. Such processes consist of two steps, namely, delineation of the pattern in a thin polymer film and transfer of the pattern into the underlying substrate using an appropriate etching technique. To obtain smaller and smaller feature sizes, the use of very thin resist layers has become necessary to avoid pattern collapse at small dimensions. The polymer sensitivity to the employed irradiation (UV, X-rays, etc.) and the etch resistance of the photoresist are significant factors that determine the quality of the photoresist.

The so-called plasma-developable resist systems generally involve a hydrocarbon polymer film containing areas that are selectively loaded with an inorganic component.[2] When placed in an oxygen plasma environment, the organic regions etch quickly, while the areas containing the inorganic component (such as silicon,[3] tin,[4,5] germanium,[6] or titanium[7]) are converted into a nonvolatile oxide. For example, selective silylation of areas is an approach to obtain etch resistance in an oxygen plasma.[8] Selective incorporation of inorganic components can be accomplished by irradiating the film and in a subsequent step treating the film with an inorganic reagent, either from solution or from the gas phase. Most of the published work that follows this general process deals with phenolic hydroxyl-containing films that react with a silylating agent to yield the corresponding silyl ether.

Multilevel resist processes have been developed to separate the imaging layer from the process etch mask. Simply stated, multilevel lithography combines the properties of the imaging layer with those of an etching barrier. Generally either random copolymers[9] or block copolymers[10] are used, which possess a monomer unit that is incorporated to provide sensitivity, while a

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monomer containing an inorganic component is added to enhance the etch selectivity.

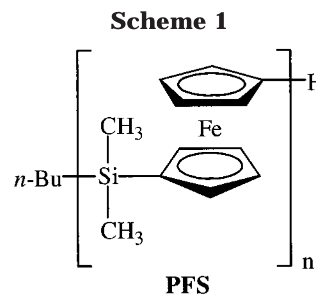
Much attention has been devoted to polymers containing inorganic components that are useful as etch barriers in multilevel applications.[11] In particular organosilicon polymers are good candidates for multilevel lithography.[12] Organic polymers are usually converted into volatile products upon exposure to oxygen plasmas, whereas in silicon-containing polymers a thin, nonvolatile silicon oxide layer is formed at the surface.[13-15] The high etch rate ratio between organic and organosilicon polymers has been frequently used to obtain high aspect ratio features in an oxygen plasma.[16]

Organometallic materials are employed for direct writing methods in lithographic applications as well. Direct writing of metallic features is possible by irradiating thin films of organometallic materials, a metal–organic cluster coordination compound, for instance with highly focused charged particle beams.[17] Irradiation of the organometallic species results in the physical removal of the organic stabilizers with concomitant formation of insoluble metallic features.

Oxygen and oxygen-containing plasmas are most commonly employed to modify polymer surfaces. Reactive ion etching can be divided into two processes, namely, chemical and physical etching.[18] The balance between these two etching mechanisms depends on many variables, such as gas pressure and composition, reactor design, and temperature.[19,20]

Pattern transfer into the substrate is frequently accomplished using fluorocarbon reactive ion etching. Fluorocarbon plasmas are extensively used to etch SiO_2 and although the process of etching with such plasmas is very complex and diverse, some general observations can be highlighted. The C/F atomic ratio of the feed gas is a crucial parameter for the nature of the plasma.[21] CF and CF_2 radicals $[CF_x]$ correlate with fluorocarbon film formation at the substrate, whereas fluorine atoms present in the plasma account for the etching of the substrate. When the C/F atomic ratio increases, relatively more CF and CF_2 radicals will be present at the expense of atomic fluorine, and the plasma becomes polymerizing rather than etching.[22] Even a very thin fluorocarbon film deposited on the substrate results in significant reduction of the SiO_2 etch rate. To suppress this so-called etch stop, the fluorocarbon gases are diluted with other gases such as oxygen.[23,24] Oxygen atoms act as scavengers for carbon and consequently a relative higher [F] (the etching component) rather than $[CF_x]$ (the polymerizing component) is obtained.

Scheme 1



This paper describes the potential of poly(ferrocenyldimethylsilane)[25,26] as an etch barrier in O_2 and CF_4/O_2 plasmas. The surface and depth profile of plasma treated poly(ferrocenyldimethylsilane) films are examined with XPS and AES depth profiling. Previously, thin films of ferrocenyldimethylsilane containing block copolymers were employed for nanolithographic applications.[27] As a proof of principle, a regular pattern of the polymer is generated by a soft lithographic method,[28] similar to microcontact printing (μCP),[29] and etched into the underlying substrate.

Experimental Section

1,1-Dimethylsilylferrocenophane was prepared as described earlier.[30] The monomer was purified by several recrystallizations from heptane at −60 °C and vacuum sublimations. Polymerization was carried out in THF in a glovebox purged with prepurified nitrogen. *n*-Butyllithium was used as initiator, and the reaction was terminated after 2 h by adding a few drops of methanol. The polymers (Scheme 1) were precipitated twice in methanol and dried in vacuo.

Thin films (approximately 60–100 nm) were prepared by spin-coating of a polymer solution in toluene onto a silicon wafer, containing its native oxide, at 4000 rpm for 30 s. The wafers were cleaned prior to spin-coating. The cleaning involved treatment for 10 min in 100% nitric acid, rinsing subsequently with deionized water, followed by additional treatment for 15 min in 70% nitric acid at 95 °C, and finally rinsing with deionized water and dry spinning.

Film thicknesses were varied by spin-casting from different concentrations of polymer solutions. Thicknesses were mea-

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sured with a Plasmos SD 2002 ellipsometer using a wavelength of 632.8 nm. The thickness was determined on 25 spots on a wafer, and the standard deviation was always less than 1%.

Microcontact printed patterns were prepared by using PDMS (poly(dimethylsiloxane)) stamps. Sylgard 184 (Dow Chemical) poly(siloxane) and curing agent were used in a ratio of 10:1 wt %. The siloxane and curing agent were poured onto a silicon master and placed in an oven at 60 °C. When cross-linking was completed the polysiloxane elastomer (PDMS) was removed from the master. The PDMS stamp was then placed on the wafer, and a drop of polymer solution in THF was placed next to the stamp. Due to capillary action, the solution diffused into the voids between the stamp and the wafer substrate. After a few minutes of contact the stamp was removed.

Reactive ion etching (RIE) experiments were carried out in an Elektrotech PF 340 apparatus. During oxygen RIE the pressure inside the etching chamber was 10 mTorr, the substrate temperature was set at 10 °C, and an oxygen flow rate of 20 cm^3/min was maintained. The power was varied between 20 and 75 W. To determine the etch rate of the organic polymers, films were etched under the conditions mentioned above for 10−20 s, and the decrease in film thickness was determined by ellipsometry. As the refractive index is changing during etching, thickness values are only approximate. The etch rate of poly(ferrocenyldimethylsilane) could be determined over longer etching times, typically 1−2 min, because of the very low etch rate. CF_4/O_2 RIE was performed at a pressure of 2 mTorr, with a substrate temperature of 10 °C. The power used was set at 20 W, which resulted in a bias voltage of approximately 160−190 V.

Silicon nitride substrates were prepared by plasma enhanced chemical vapor deposition (PECVD) in an Electrotech PF 310 apparatus. Typically thicknesses of approximately 100 nm were prepared.

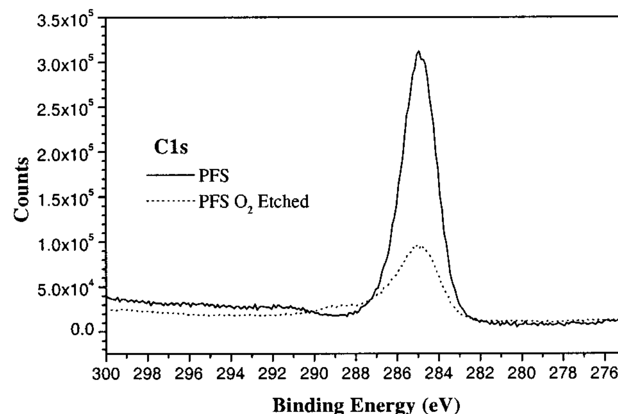
Atomic Force Microscopy (AFM) experiments were performed on a Digital Instruments NanoScope IIIa. A standard Si_3N_4 tip was used, and the images were acquired in the contact mode with a scan rate of 1 Hz and contact reduced to the minimum necessary to maintain feedback.

Both etched and unetched 60 nm thin films of PFS homopolymer were studied by X-ray photoelectron spectroscopy (XPS). Measurements were performed with a Kratos XSAM-800 spectrometer using a Mg Kα X-ray source (1253.6 eV). The input power was set at 150 W (15 kV and 10 mA) and the hemispherical analyzer was placed perpendicular to the sample surface. Survey scans (0−1100 eV) were recorded to qualitatively determine the elements present. The atomic concentrations of carbon (1s), oxygen (1s), silicon (2p), and iron (2p) were determined from the relative peak areas calculated by numerical integration of the detailed scans (20−30 eV windows) and corrected for relative XPS sensitivities.[31]

Auger electron spectroscopy (AES) was performed at an electron energy of 10 keV, with an electron current of 1 A. Sample sputtering for depth profiling was accomplished with a 3 keV argon ion beam over a 2 × 2 mm^2 raster. Detected elements were oxygen (KVV transition, 490−525 eV), silicon ($KL_{23}L_{23}$ transition, 1585−1625 eV), carbon (KVV transition, 250−285 eV), and iron (L_3VV transition, 680−715 eV).[32] The thickness of the O_2-RIE treated poly(ferrocenyldimethylsilane) film that was used for the AES measurement was measured by a surface profiler (Sloan Dektak 3030).

Results and Discussion

Oxygen Reactive Ion Etching. Figure 1 shows the XPS C 1s (284.9 eV) and O 1s (531−532 eV) spectra of PFS films prior to and after oxygen reactive ion etching.



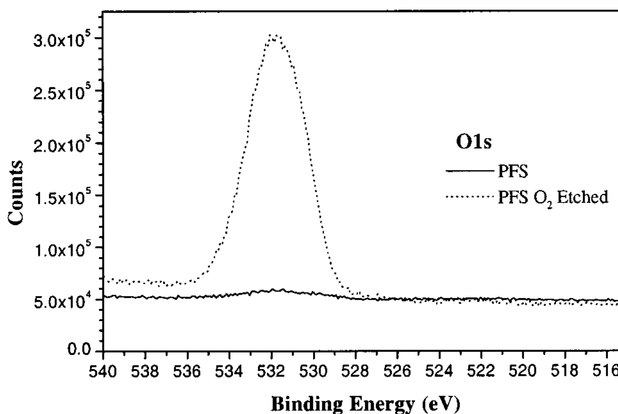


Figure 1. XPS spectral details of poly(ferrocenyldimethylsilane) (PFS) thin films for carbon (upper, C 1s) and oxygen (lower, O 1s). Upon oxygen etching, the carbon concentration decreased while the oxygen concentration increased.

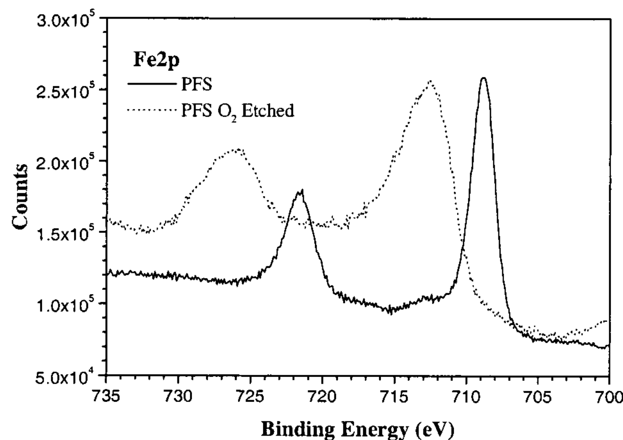


Figure 2. XPS spectra of Fe2p of the as cast film (solid line) and the O_2-RIE treated film (dashed line).

It is clear that the carbon concentration decreased at the surface upon oxygen etching, while the oxygen concentration increased. The aromaticity was destroyed during the oxidation, as inferred from the disappearance of the small shake-up peak for the C 1s signal at about 291 eV. This is consistent with the formation of a thin oxide layer, from which carbon atoms are largely expelled.

The XPS spectra for iron are shown in Figure 2. The iron signals at 708.8 eV ($2p_{3/2}$) and 721.5 eV ($2p_{1/2}$) have not decreased in magnitude as significantly as the carbon signal has. The relative atomic concentration of

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Table 1. Atomic Concentrations [with Sensitivity Factors between Brackets[31]] for PFS Homopolymer Films before and after O_2-RIE

element	PFS homopolymer	PFS homopolymer O_2 etched
C 1s [0.25]	85.1	33.3
O 1s [0.66]	1.9	41.8
Si 2p [0.27]	6.1	8.0
Fe 2p [3.0]	6.9	16.9

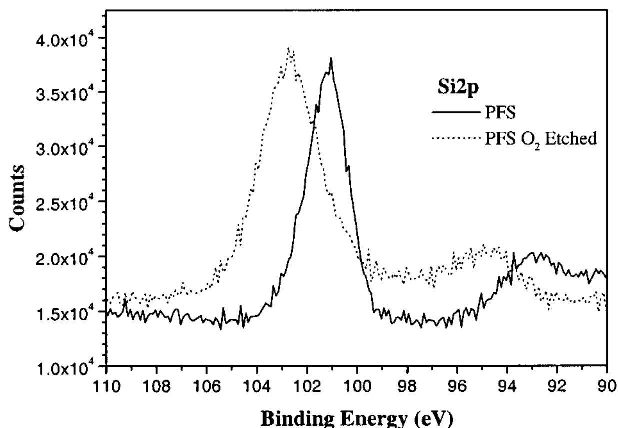

Figure 3. XPS spectra of Si 2p of the as cast film (solid line) and the O_2-RIE treated film (dashed line).

iron has even increased (see Table 1). The position of the Fe $2p_{3/2}$ peak at 708.8 eV was found at an energy close to the value of 707.8 eV for ferrocene.[31] Furthermore, upon O_2-RIE the iron signals shifted to higher binding energies of 712.6 eV ($2p_{3/2}$) and 726.0 eV ($2p_{1/2}$), and the peaks became broader compared to the iron signals of the untreated film. The shift to higher binding energies for the Fe electrons indicates a higher oxidation state.

The XPS data for silicon showed comparable trends as were discussed for iron. In the XPS spectra for silicon (Figure 3), a shift to higher binding energy was observed as a result of the oxygen plasma treatment (from 101.1 to 102.7 eV), which is indicative of the formation of an oxide. Before oxidation, the Si 2p peak position at 101.1 eV is near the value for Me_4Si (100.5 eV) and Ph_4Si (101.2 eV).[31] The peak position of silicon after the O_2-RIE treatment at 102.7 eV is about midway between the expected positions for siloxane (102.4 eV) and SiO_2 (103.4 eV).[31]

The atomic concentrations according to the XPS measurements, prior to and after the O_2-RIE treatment, are given in Table 1. For the PFS homopolymer, concentrations for C:Si:Fe of 12:0.86:0.97 are found, which is close to the theoretical relative amounts of 12:1:1 ($C_{12}H_{14}FeSi$ for a repeat unit). Following O_2-RIE the oxygen concentration increased significantly, while the carbon concentration decreased. Interesting phenomena can be seen, if one considers the relative amounts of the different elements. Both the Si/C and the Fe/C ratio increased upon oxygen etching, indicating that Si and Fe are more stable toward removal using an oxygen plasma. Furthermore, the Fe/Si ratio increased, suggesting that Fe is more stable than Si toward RIE treatment using oxygen plasma. Although silicon-containing polymers were mainly employed to enhance stability toward oxygen plasma treatments, these results indicated that the incorporation of other inorganic elements, such as iron, can significantly improve the etch resistance in oxygen plasmas.

From the XPS results it is clear that an oxide layer forms at the surface of poly(ferrocenyldimethylsilane) upon oxygen plasma treatment. The presence of such a nonvolatile oxide results in relatively low etching rates in O_2-RIE compared to common organic polymers.[27] The difference between etching rates for organic polymers and poly(ferrocenyldimethylsilane) depends strongly on the operational settings. As mentioned before, the etching process can be divided into two parts, namely chemical and physical etching. Chemical etching is highly selective, since it removes organic polymer quickly whereas it forms a nonvolatile oxide layer at the surface of poly(ferrocenyldimethylsilane). Physical etching on the other hand is almost nonselective and becomes more pronounced when the bombardment of ions takes place at higher velocity. Therefore, physical etching is stronger at higher power settings, and correspondingly the chemical etching effect is more effective at relatively low power settings.

The etching rates were determined for poly(styrene), poly(isoprene), and poly(ferrocenyldimethylsilane) at a fixed pressure of 10 mTorr and an oxygen gas flow of 20 cm^3/min, while varying the applied power, which influences the acceleration voltage of the ions toward the surface. A significant influence of the applied power could be observed. The etching rate ratios increased from approximately 20:1 to almost 50:1 for organic polymers compared with poly(ferrocenyldimethylsilane) as the power was decreased from 75 to 20 W. This large increase in etch selectivity can be ascribed to the increased influence of the selective chemical etching compared to the nonselective physical etching.

From Auger electron spectroscopy (AES), using argon ion-sputtering depth profiling, the thickness of the surface oxide layer can be estimated. The Auger electrons of the elements of interest can be measured as an argon ion beam is slowly milling (~1 nm/cycle) through the film. A thin poly(ferrocenyldimethylsilane) film was exposed to an O_2-RIE treatment for 15 s and the film composition was measured as a function of sputtering cycles. If the sputtering rate by the argon ion gun is constant through the film, the sputtering time can be correlated with the *z*-distance in the film if the thickness is known.

The AES depth profile shown in Figure 4 confirms the observations made by XPS. The film thickness of the etched polymer layer was approximately 106 nm, as determined by profilometry. In the AES spectra, the first sputtering cycle corresponds to the sample surface, and the increase of the silicon signal around cycle 90 indicates the underlying silicon substrate. In general, however, the sputtering rate varies with composition and therefore the relation between sputtering time and depth becomes nonlinear.[33] Assuming a constant sputtering rate for this bilayer system, a thin oxide-rich layer of approximately 10 nm is present at the surface. It is interesting to compare the composition at the surface (sputtering cycle 0) with the internal composition of the film. From this, it can be seen that relatively less carbon and a significant amount of oxygen was present at the surface oxide layer compared to the film interior. Due to the oxidation at the surface, a large

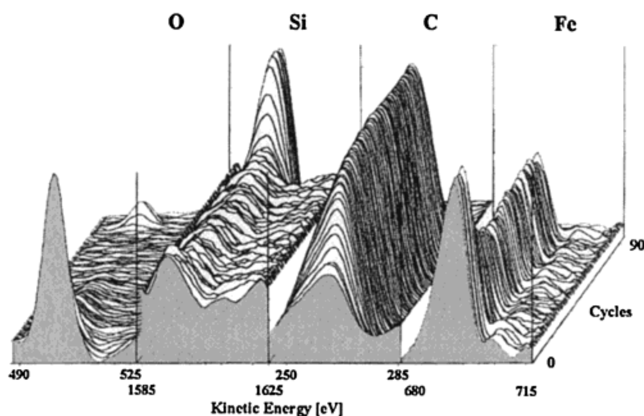

Figure 4. Auger electron spectroscopy (O KVV, C KVV, Fe L_3VV, and Si $KL_{23}L_{23}$) depth profile of an oxygen etched film of poly(ferrocenyldimethylsilane) of 106 nm. Cycles start at the surface and end at the substrate.

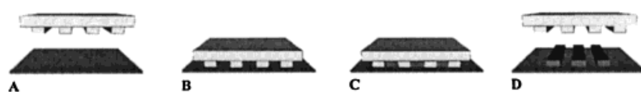

Figure 5. Schematic of the procedure used in MIMIC. A PDMS stamp is placed onto a substrate (A and B). A drop of the polymer solution is placed in contact with the stamp and substrate, and the channels are filled by capillary action (C). After evaporation of the solvent, the stamp is removed and the polymer remains on the substrate (D).

amount of carbon is expelled from and oxygen is added to the surface. Furthermore, the amount of silicon at the surface seems to be approximately equal compared to the amount below the oxide layer of the film. As was also shown in Table 1, more silicon was removed from the surface compared to iron after oxygen plasma treatment. This is also clear from Figure 4, where the surface layer shows a higher concentration of iron compared to the bulk of the film.

Carbon Tetrafluoride Reactive Ion Etching. Radio frequency discharges in low-pressure fluorocarbon gases are often used for etching silicon, silicon oxide, and silicon nitride. The gas mixtures are composed of CF_4, CHF_3, C_2F_6, etc. By adjusting the composition of the gas, the nature of the plasma can be dramatically changed.[22]

Carbon tetrafluoride (CF_4) has the most pronounced etching characteristics of the gases used on materials that are reactive with fluorine atoms. Its decomposition in the plasma is characterized by the highest concentration of fluorine atoms (F) and the lowest concentration of CF and CF_2 radicals. If the F/C atomic ratio of the feed-in gas decreases, the concentration of CF and CF_2 radicals will be higher at the expense of F, and the plasma becomes "polymerizing" and hence protective rather than "etching". The deposition of polymer film on silicon[34] protects the substrate from chemical etchants (F), thus stopping the etching. To reduce the deposition of fluorocarbon polymer during the reactive ion etching treatment, the CF_4 gas was diluted with oxygen (20 vol % CF_4 in the gas mixture).[21] The addition of O_2 to a fluorocarbon etching plasma usually results in a significant increase in the etch rate of Si, as well as reduced fluorocarbon polymer deposition.[23]

A pattern was generated by a microcontact printing technique known as micromolding in capillaries (MIMIC).[35] To briefly describe this process; in MIMIC a patterned poly(dimethylsiloxane) (PDMS) stamp is placed on a clean silicon substrate. When a drop of the polymer solution in THF is placed next to the PDMS stamp, the capillary force transports the polymer solution into the pattern. After several minutes the solvent is evaporated or diffused into the stamp, and the stamp can be removed, leaving the polymer on the substrate (Figure 5).

The MIMIC process can be used to transfer a polymer pattern on a solid substrate consisting of parallel lines. The AFM image in Figure 6 shows a homopolymer film pattern of a MIMIC printed surface structure of PFS, both before and after CF_4/O_2-RIE treatment. The employed plasma gas consisted of 20 vol % CF_4 and 80 vol % O_2. The pressure inside the etching chamber was kept constant at 2 mTorr, with a gas flow of 5 cm^3/min. Applying a power of 20 W resulted in a bias voltage of approximately 160−190 V.

The pattern transfer clearly demonstrates the potential of the ferrocenyldimethylsilane polymer as an etch resist. The features that are present in the original line pattern can still be observed after the CF_4/O_2 plasma treatment. The shapes of the polymer domains have not

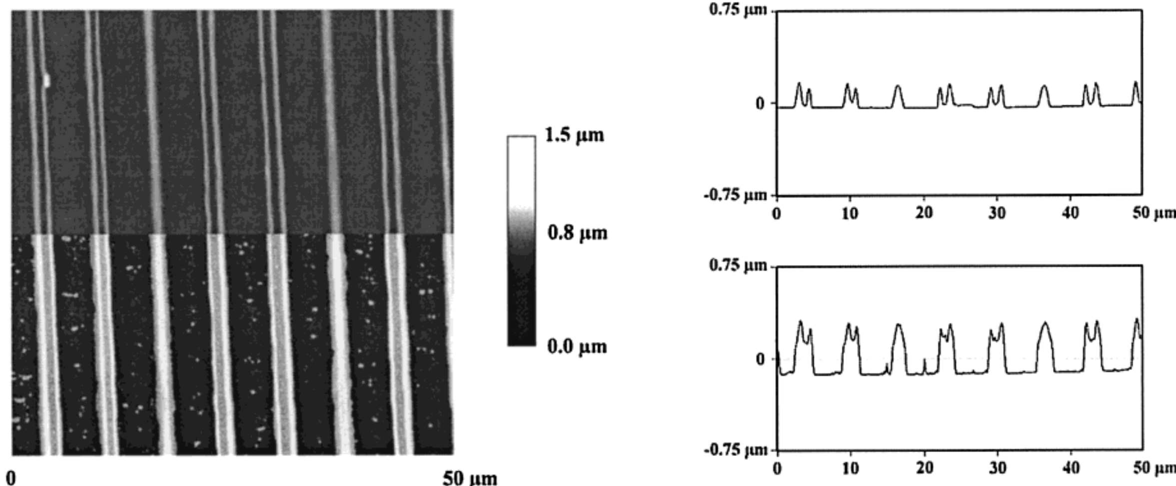

Figure 6. AFM images (left) and single line scans (right) of a ferrocenyldimethylsilane homopolymer pattern, before and after CF_4/O_2-RIE treatment. The top half of the AFM image corresponds to an unetched area and the bottom half of the image displays the etched area. The sample was etched for 10 min, which led to an increase in the domain height by approximately 200 nm.

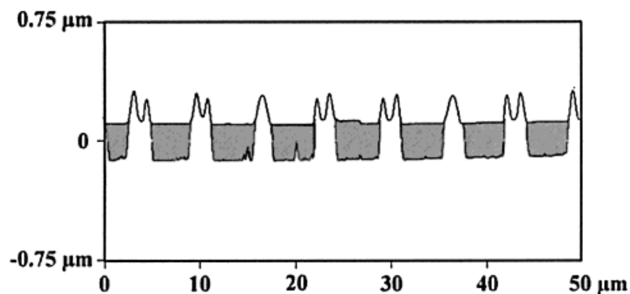

Figure 7. AFM section analysis, illustrating the etched substrate as a result of a CF_4/O_2-RIE treatment. During 10 min of etching, approximately 200 nm of silicon was removed, indicated by the gray area.

changed during etching. Therefore, the section analysis from the AFM images can be superimposed onto each other, which results in a clear illustration of the amount of silicon that was removed by the reactive ion etching treatment. Figure 7 displays an overlay of the line scans from the unetched and etched samples. The gray area in this figure corresponds to the removed silicon. Approximately 200 nm of silicon was removed in 10 min, resulting in an etch rate of 20 nm/min, which is about equal to the etch rate of silicon nitride under similar conditions. No decrease in the film thickness of poly(ferrocenyldimethylsilane) was observed after etching times exceeding 10 min.

The AFM images and line scans indicate that poly(ferrocenyldimethylsilane) exhibits good dimensional stability during the plasma treatment. Although no effort was taken to optimize and alter the etching conditions, it has been clearly shown that poly(ferrocenyldimethylsilane) has promising properties to function as an etch barrier.

Conclusions

The potential of poly(ferrocenyldimethylsilane) as etch resistant polymer has been demonstrated under reactive ion etch conditions. Upon exposure to an oxygen plasma, an approximately 10 nm thin oxide layer was formed at the surface. The nonvolatile oxide gave rise to relatively low etching rates in oxygen plasmas compared to organic polymers. Due to the presence of iron in the polymer and its oxide layer, low etching rates were also obtained when fluorocarbon plasmas were applied. It was possible to increase the aspect ratio of the features by etching into the substrate while the masking layer was not affected (i.e., very high selectivity toward silicon and silicon nitride substrates). Masking layers with such high etching barriers are potentially useful for very thin resist layer applications or for high aspect ratio structures. Such properties are preferable for high-density imaging and cannot be expected from etch barriers containing silicon only. The etching resistance has been demonstrated for PFS, so a challenge is left to combine the etching properties with developable species. For example, the preparation of block copolymers consisting of poly(ferrocenyldimethylsilane) combined with a radiation sensitive block might result in a bilevel resist.[10]

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