

# Reactive Ion Etching of Silicon Containing Polynorbornenes

## Qiang Zhoo\* and Paul A. Kohl\*\*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, USA

#### ABSTRACT

Silyl ether modified polynorbornene is a new class of dielectric polymer materials of interest in electronic packaging and other applications. This work is focused on the reactive ion etching of polynorbornenes in oxygen, oxygen/fluoroform, and oxygen/fluoroform/argon plasmas. The etch rate, amount and nature of the residue, and etch undercut rate have been investigated for different plasma parameters, such as pressure, plasma power, and gas composition. X-ray photoelectron spectroscopy and scanning electron microscopy were used to characterize the residue. Several techniques were used to reduce the etch residue and undercut.

#### Introduction

High performance interconnections and packages are required to meet the needs of advanced microelectronic devices. Higher speed interconnections can be achieved by lowering the dielectric constant of the insulation. The lower dielectric constant reduces capacitive coupling and minimizes cross talk between adjacent metal lines, which is crucial for devices with feature sizes below 0.25 µm. Currently, the dominant insulator material for integrated circuits is silicon dioxide deposited by plasma enhanced chemical vapor deposition (PECVD), which has a dielectric constant of PECVD 3.9 to 4.2. This value may be lowered to 3.5 by fluorinating the silicon dioxide resulting in a silicon oxyfluoride.2 There is a great deal of interest in lowering the dielectric constant to less than 3.0, primarily through the use of organic polymers. Polymeric materials based on polyimide and benzocyclobutene (BCB) have demonstrated dielectric constants lower than 3.0.3-5

There is considerable interest in the development of new, cost effective, high performance polymer dielectrics for packaging applications. Recently, polynorbornenes have been developed for 193 nm photoresist applications<sup>6,7</sup> and as interlevel dielectric materials. 8,9 Polynorbornenes (trademarked under the name of  $Avatrel^{\text{TM}})$  have been synthesized via a new and unique transition metal catalyzed polymerization from norbornene-based monomers,' which are derived from the Diels-Alders adducts of cyclopentadiene. A unique catalyst system and a broad selection of monomeric units permits wide flexibility in producing a range of different structures and properties through a relatively easy synthetic route. Alkoxy and alkyl side groups give polynorbornenes excellent properties and make them attractive for use in interlevel dielectric applications. Avatrel<sup>TM</sup> has a low dielectric constant (2.4-2.5), low moisture absorption (< O.1%), and excellent adhesion to metals.9

Reactive ion etching (RIE) is a well-established technology in the semiconductor industry for etching polymeric dielectrics. Etching hydrocarbon polymers by RIE is usually performed in an oxygen plasma, and forms volatile and thermodynamically stable products such as CO, CO,, and  $\rm H_2O.^{10,11}$  Polyimide etching for multilevel interconnections in very large scale integration (VLSI) circuits and advanced packages has been reported.' However, silicon

\* Electrochemical Society Student Member.

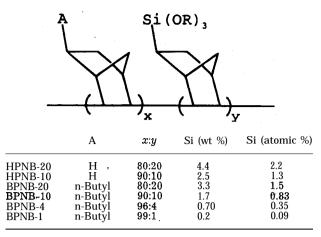
\*\* Electrochemical Society Active Member.

containing polymers<sup>12,13</sup> such as silylated photoresist<sup>15,16</sup> and benzocyclobutene<sup>4</sup> are more difficult to etch, because nonvolatile silicon oxide is formed during the etching process in an oxygen plasma. Efficient and complete oxygen etching of silylated photoresist<sup>17</sup> and silicone modified polyimide<sup>18</sup> has been reported with a magnetic field enhanced RIE etcher. The removal of the resulting silicon oxide can also be achieved by addition of a small amount of a fluorine containing molecule into the oxygen plasma. Moreover, the concentration of fluorine in the plasma has been found to play an important role on the smoothness of the etched polymer surfaces. <sup>19,20</sup>

In this study, the focus has been on the RIE behavior of a variety of polynorbornenes containing trialkoxy silyl groups in an oxygen, oxygen/fluoroform, or oxygen/fluoroform/argon plasma. The etch rate, residue, and undercut have been investigated as a function of plasma conditions, such as pressure, plasma power, and gas composition. To reduce the RIE undercutting and etch residues, several techniques including argon addition, use of dummy wafers, and postetching treatment were used.

#### **Experimental**

A series of polynorbornenes have been synthesized with different alkyl groups (BF Goodrich Company, Brecksville, OH). Polynorbornene (HPNB) and polybutylnorbornene (BPNB) containing trialkoxy silyl groups were investigated. The chemical structures are shown in Fig. 1. The silicon content of each was from 0.7 to 4.4 wt %. All samples were spin-coated on 100 mm diam (10 0) silicon wafers sputtered with Cr/Au (10/100 nm). The polymer film thickness was approximately 5 to 6 µm. The wafers were baked at 300°C for 1 h under a nitrogen atmosphere prior to etching. Silicon oxide, deposited by PECVD using 400 sccm  $\mathrm{SiH_4/N_2}$  (2/98) and 900 sccm  $\mathrm{N_2O}$  at 900 mTorr and 120°C, was used as the hard mask in the polynorbornene etching experiments. The typical thickness of the hard mask was 1.0 µm. The silicon oxide mask was patterned using Shipley 1827 photoresist. The photoresist pattern was transferred to the silicon dioxide by wet etching with a commercially available 6:1 buffered oxide etching (BOE) solution. The photoresist was then removed with acetone and rinsed with deionized water, and the wafer was cleaved into 1 cm<sup>2</sup> pieces for the etching experiments. To evaluate the RIE undercut, the pattern was transferred from the photoresist



<sup>a</sup> H is not counted to calculate the Si atomic percentage.

Fig. 1. Chemical structure of polynorbornenes.

to the silicon dioxide by RIE using 45/5 sccm fluoroform/oxygen at 100 mTorr and 300 W. This produced a more vertical sidewall in, the silicon dioxide mask layer.

All RIE experiments were performed in a Plasma-Therm 700, parallel-plate, reactive ion etcher (13.56 MHz). The temperature of the lower electrode was maintained at 35°C. The flow of the etching gases were controlled by mass flow controllers and was premixed before being introduced into the reaction chamber. Loading effects as a result of the number of samplesand sizes were not taken into account. The etched depth was measured with a Tencor Alpha-Step 500 profiler after removal of the hard mask by BOE. A scanning electron microscope (Hitachi S-2700) was used to analyze the RIE residues and the undercut through cross section observation. X-ray photoelectron spectroscopy (XPS) (Surface Science SSX-100) was used to characterize the elemental composition of the residue and investigate the cleaning efficiency of the postetching treatments. All the samples examined by XPS were sputter cleaned with an argon ion gun for 2 min in the XPS to remove atmospheric contamination. Control samples showed that longer sputtering times did not improve the surfaces. The sputtering rate was measured to be 3 nm/min on a polyimide film.

## Results and Discussion

*Oxygen RIE* behavior.-The RIE behavior of HPNB and BPNB in an oxygen plasma is shown in Fig. 2 for polymers with different concentrations of silicon. The pressure was 300 mTorr and the power was 400 W for each of the six different polynorbornenes. The percentage of silylated monomer in the polymer is shown as the number following

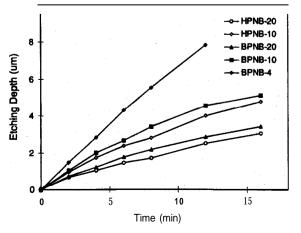


Fig. 2. Etch depth for polynorbornenes as a function of time. Etching conditions: 300 mTorr, 50 sccm oxygen, and 400 W.

the abbreviation (e.g., BPNB-4 has 4% of the monomer units modified with triethoxy silyl ether and 96% with butyl). The etch rate decreased in the order: BPNB-4 >BPNB-10 >HPNB-10 >BPNB-20 >HPNB-20. This shows that the higher the silicon content, the slower the etch rate. A porous, protective silicon oxide layer has been identified to be accumulating on top of the polymers as etching progresses. The porous layer can be removed by rinsing the sample with BOE, leaving a rough surface. The higher the silicon content in the polymer, the more silicon oxide remained on the surface after RIE in the oxygen plasma. The rate of etching became nonlinear with the time for thicker polymer films because of the accumulation of silicon dioxide on the surface. However, the HPNB-4 etch rate remained constant throughout the 12 min required to etch the 8 µm film. Scanning electron microscopy (SEM) observation of completely etched BPNB-4 still shows a substantial amount of silicon oxide based residue remaining. The constant etch rate for HPNB-4 indicates that the erosion rate of silicon dioxide by sputtering is greater than the accumulation rate of the silicon oxide. At a pressure of 300 mTorr, sputtering is insignificant, and most likely does not result in substantial removal of silicon oxide from the etching surface. Thus, it appears that the constant etch rate is due to the inability of the accumulated silicon oxide to protect the polymer surface from etching.

XPS analyses of the polynorbornene surfaces after oxygen etching are presented in Table I. The RIE was performed at a flow rate of 50 sccm oxygen, 400 W rf power, and 300 mTorr pressure for 4 min. The 4-BPNB films were not completely etched through. The elemental analysis of the surface contained oxygen, silicon, carbon, fluorine, and aluminum. Hydrogen is not detectable by XPS. Although the chamber was cleaned in pure oxygen etching for 20 min prior to its use, the fluorine residue is most likely a result of contamination from previous etching experiments in the chamber. The aluminum contamination was probably from erosion of the chamber. The elemental percentages shown in Table I are similar except for the BPNB-1 surface. Although a constant etch rate was observed for BPNB-4 in Fig. 2, the etched surface had the same composition as the other BPNB materials with higher silicon content. This indicates that the silicon oxide layer formed on the BPNB-4 surface is not thick enough to slow the etch process. The BPNB-1 surface, however, has a significantly lower silicon and oxygen content and a much higher carbon content compared to the other three BPNB surfaces. This demonstrates that an incomplete silicon dioxide layer is formed on the surface of the BPNB-1 with only 0.2 wt % silicon. After the full thickness of the BPNB-1 film was etched, it is noted that the elemental composition of the etch residue was close to the other BPNB materials containing more silicon.

Figures 3 and 4 present the dependence of the etch rate of polynorbornenes on plasma pressure and power in an oxygen plasma. The etch rates of six polynorbornenes are in the reverse order of their silicon content for both constant pressure (300 mTorr in Fig. 3) and constant power (300 Win Fig. 4) conditions. In Fig. 3, higher power increased the RIE etch rate for each polynorbornene by increasing the number of energetic ions and active neutral species to the surface. The

Table I. Elemental composition (atomic %) measured by XPS° for polynorbornenes after RIE in pure oxygen plasma.<sup>b</sup>

Polymer	С	0	Si	F	Al
BPNB-1 BPNB-4 BPNB-10 BPNB-20 BPNB-1#	38 3 2 2 2 4	35 56 56 59 58	19 36 37 34 24	2 4 3 3 6	6 2 2 2 2 9

<sup>&</sup>lt;sup>a</sup> The samples were sputter cleaned by argon ion gun for 2 min

before XPS analysis.

BIE conditions were 50 sccm oxygen, 400 W, 300 mTorr for 4 min. The etching is complete except for the BPNB-1 entry marked "#".

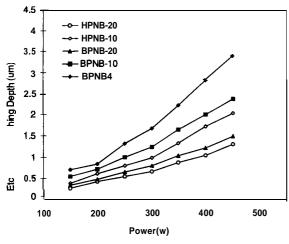


Fig. 3. Etch depth for polynorbornenes as a function of power. Etching conditions: 300 mTorr, 50 sccm oxygen, and 4 min.

pressure effect shown in Fig. 4 is more complicated. At the low pressure, the etch rate is less because the number of oxygen ions and radicals are fewer, although ion bombardment is enhanced due to the higher kinetic energy of the ions. At pressures above 300 mTorr, the ionic bombardment decreases significantly, and causes a lower etch rate. It is noted that that the etch rate dependence of silicon oxide is different from that of organic polymers. The etch rate of silicon oxide by RIE in oxygen plasma increased with a decrease in pressure, since only the sputtering mechanism is responsible for its etching. The difference in pressure dependence of the etch rates between polynorbornenes and silicon oxide indicates that the protective silicon oxide layer formed on polynorbornenes is not compact enough to prevent the etching of the underlying polymer.

Oxygen/fluoroform RIE behavior.-In order to remove the silicon oxide formed on the surface during the RIE and allow the underlying polymer to be etched, fluorine containing compounds were added to the plasma. In these experiments, fluoroform was used. Etch rate curves for the polynorbornenes as a function of oxygen/fluoroform ratio are shown in Fig. 5. The etching conditions for the experiments were 50 sccm total flow rate and 300 W rf power at 300 mTorr for 2 min. Unlike BCB (14.4 Si wt %), whose etch rate increased significantly with at least 2.5 sccm tetrafluoromethane, 20 polynorbornenes have a significant increase in etch rate increase with just 1.5 sccm fluoroform due to their lower silicon content. The maximum etch rate was found at about 3 to 5 sccm fluoroform with a sharp decrease

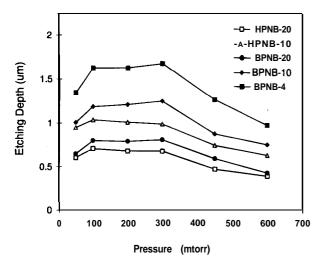


Fig. 4. Etch depth for polynorbornenes as a function of pressure. Etching conditions: 50 sccm oxygen, 300 W, and 4 min.

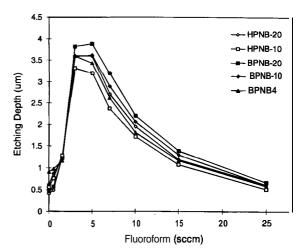


Fig. 5. Etch depth for polynorbornenes as a function of oxygen/fluoroform mixture composition. Etching conditions: 300 mTorr, (50 - x)/x sccm oxygen/fluoroform, 300 W and 2 min.

in etch rate at fluoroform flow rates greater than 5 sccm. The maximum etch rate for BCB was found at a much higher tetrafluoromethane concentration."

As shown in Fig. 5, the six polynorbornenes have about the same etch rate at a flow rate of 1.5 sccm fluoroform (48.5 sccm oxygen) independent of their silicon content. This indicates that 1.5 sccm fluoroform is sufficient to etch the silicon oxide formed on the surface, even for HPNB-20, which contained the highest silicon content (4.4 wt %). A partially etched BPNB-20 surface was examined by XPS and was found to contain only about 10% Si. This is significantly lower than the silicon content (59%) for the BPNB-20 surface after RIE in pure oxygen plasma. The partially etched surfaces of polynorbornenes in oxygen/fluoroform plasma with more than 1.5 sccm were also examined, and were found to contain no silicon. The increase in etch rate with fluoroform flow rate up to its maximum value at 3 to 5 sccm, is most likely due to a synergistic effect of fluorine in an oxygen plasma. First, the addition of fluorine compounds to the oxygen plasma increases the electron energy and density which provide additional oxygen molecule dissociation. Second, fluorine passivates the reactor walls and decreases the oxygen recombination rate on the wall surfaces. Last, fluorine atoms abstract H from the organic polymer surface by the formation of HF. This renders the remaining carbon atoms more susceptible to attack by oxygen atoms. Fluoroform flow rates greater than 5 sccm dilute the oxygen and cause a decrease in etch rate. Additionally, a higher fluoroform concentration enhances the formation of fluorocarbon polymer in the plasma, and also diminishes the etch rate.

The order of the etch rate for the polynorbornenes (Fig. 5) is different from that in pure oxygen. At lower fluoroform flow rates (<1.5 sccm), the etch rates for the different polynorbornenes have the same order as that in pure oxygen etching, which were strongly influenced by the silicon content in the polymers. At higher fluoroform flow rates (>5 sccm), the etch rates decrease in the order BPNB-20 >BPNB-10>HPNB-20>BPNB-4>HPNB-10. At high fluoroform flow rates, the identity of the pendent groups and their amounts, not the silicon content of the polynorbornenes, are the primary factors influencing the etch rate. Based on the results shown in Fig. 5, the introduction of the alkoxy silyl and alkyl groups make polynorbornenes more susceptible to attack by the active species in the plasma. Thermal analysis also shows a lower thermal stability when these groups are introduced in the polymer structure.21

Figures 6 and 7 show the dependence of the etch rate of polynorbornenes on the plasma pressure and time in an oxygen/fluoroform (47/3 sccm) plasma, respectively. The effect of power in a oxygen/fluoroform (47/3 sccm) plasma is not shown, since it was very similar to the relationship

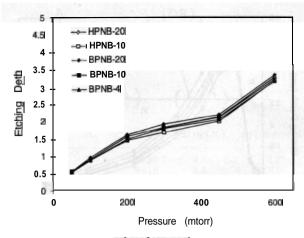


Fig. 6. Etch depth for polynorbornenes os a function of pressure. Etching conditions: 47/3 sccm oxygen/fluoroform, 300 W, and 1 min.

in pure oxygen as shown in Fig. 3. However, with an increase in pressure, the etch rates of the polynorbornenes are observed to increase as shown in Fig. 6. This is different from what is shown in Fig. 2 under pure oxygen conditions. This result indicates that a chemical reaction mechanism dominates the etching process in t.he oxygen/fluoroform (47/3 sccm) plasma. The etch rates at 100 mTord shown in Fig. 7 are relatively constant without a steep rise, as is observed in Fig. 4, in a pure oxygen plasma. This demonstrates the rapid removal of silicon oxide from the etched surface by the addition of the fluoroform. The characteristic chemical etching mechanism in the oxygen/fluoroform plasma is also demonstrated by an undesirable undercut of the masked region.

After reaching the etching end point, the etched surfaces of polynorbornene were examined by SEM. Typical SEM pictures of a gold substrate surface in a 47/3 sccm oxygen/fluoroform RIE at 300 W and different pressures are shown in Fig. 8. The two types of residues observed are islandlike particles, and a fiberlike residue depending on the pressure. At pressures above 300 mTorr, an islandlike residue is observed. The size of the islandlike residue particles became smaller with the pressure increase. Etchings at less than 100 mTorr produced a fiberlike residue on the substrate surfaces. Similarly, an increase in the fiberlike residue was observed on surfaces due to a decrease in etching pressure. The fiberlike residue left behind by etching at low pressure (50 mTorr) was not removed with additional etch time at high pressure in a oxygen/fluoroform plasma (600 mTorr). Also, it was found that both islandlike and

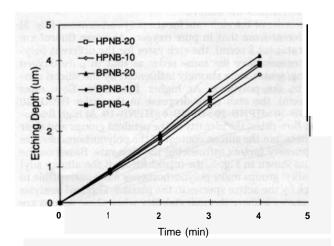


Fig.7. Etch depth for polynorbornenes as a function of time. Etching conditions: 47/3 sccm oxygen/fluoroform, 100 mTorr, and 250 W.

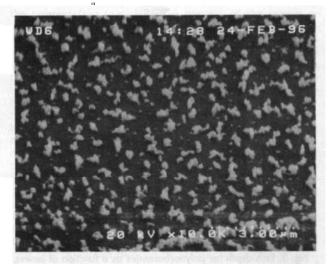




Fig. 8. SEM observation of BPNB-10 surfaces after etching under 47/3 sccm oxygen/fluoroform at 300 W and (a, top) 300 mTorr or (b, bottom) 600 mTorr.

fiberlike residues were not attacked in a pure oxygen or hydrogen plasma. In the literature, oxygen and hydrogen plasmas were reported to remove fluorocarbon residue on reactive ion etched silicon surfaces."". Attempts were made to dissolve the etch residue by rinsing with water, acetone, 6:1 BOE, or 2 N HCII solution for 2 min. Water and acetone were found to have little effect on the residue. BOE and 2 N HCII solutions were found to be effective in removing the residue. Generally, rinsing with a 2 N HCII solution gives somewhat better results than BOE. For fiberlike residue formed at low pressure RIE, 6:1 BOE, and 2 N HCII solutions change the shape of the fiberlike residue and remove most of the material. For islandlike residues formed at high pressure, rinsing with BOE and HCII solutions produced very clean surfaces as observed in an SEM.

XPS analysis was used to characterize the elemental composition of etched residue and postcleaning surfaces of the polynorbornene after oxygen/fluoroform etching. Table II presents the XPS results for BPNB-10 etched in a 47/3 sccm oxygen/fluoroform plasma at 300 W and 100 mTorr. The untreated etch residue surface consists of mainly fluorine and aluminum with a small amount of carbon and oxygen. The detection of gold indicates that the etching was complete, and the substrate was observed. Aluminum contamination is the result of back sputtering of the aluminum electrodes and etching chamber. XPS results indicate that aluminum fluoride is formed on the etched surface in an oxygen/fluoroform plasma. The unetchable aluminum fluoride is responsible for the formation of the residue at different etching conditions. At a higher pressure, isotropic chemical etching dominates and the polymer under the alu-

Table II. Elemental composition (atomic %) measured by XPS¶ for poiynorbornene (BPNB- 10) after RIE in pure oxygen/fluoroform

Postcleani	ng C		O	Si	F	Al	Au
None H.O Acetone	29	1	11 13	0	38 19 21	21 8 0	22 30 28 58
HCl	26	1	5	U	0	U	69

<sup>&</sup>quot;The samples were sputter cleaned by argon ion gun for 2 min before XPS analysis.

RIE conditions 47/3 sccml oxygen/fluoroform, 300 W, 100 mTorr and etching time is long enough to reach thr end point.

minum fluoride, which leads to formation of the islandlike residue, can be removed. In contrast, at low pressure, etching is enhanced by ionic bombardment and becomes more directional. Aluminum fluoride on the etched surface functions as a micromask, protecting the underlying polymer materials and a fiberlike residue is formed. Rinsing the etched surfaces with water and acetone leaves less fluorine and aluminum. but more gold (the substrate surface below the polymer) and carbon as measured by XPS. However, the total amount of residue was not found to decrease as seen by SEM examination. XPS examination of the etched surfaces after BOE and HCI rinsing showed a significantly different. elemental composition. The HCl solution completely removed the fluorine and aluminum from the surface and increased the gold signal from 22 to 69%. This result is in good agreement with the SEM observations, where the HCI solution provided the best postcleaning process with etched surfaces.

The RIE platter can hold four 100 mm diam wafers. To investigate the source of the aluminum contamination, the powered electrode was covered by four bare silicon wafers, where the area of the aluminum exposed to the plasma was reduced by 80%. Typical SEM images of etch residue formed when the dummy wafers were used are shown in Fig. 9. Less residue was observed in Fig. 9 compared to Fig. 8, for the same conditions. This demonstrates that the back sputtering of the powered electrode is a major contributor to the formation of the residue compared to the other aluminum sources, including the upper ground electrode and the sidewalls of the chamber. In the RIE experiments, the dc bias of the rf powered electrode was typically 300 to 400 V, which produces energetic ions and ion bombardment of the powered electrode. Etching in a high density plasma etcher with lower dc bias may reduce the back sputtering of the powered electrode and alleviate the residue formation.

Oxygen/fluoroform/argon RIE behavior.-As shown in the last section, the addition of fluorine compounds to the oxygen plasma greatly enhances the chemical etching mechanism and causes significant etch undercut. Figure 10 is an SEM cross section of polynorbornene etched in an oxygen/fluoroform (47/3 sccm) plasma. The extent of the undercut was characterized by the ratio between the horizontal etch depth X and the vertical etch depth Y. For BPNB-4 etched in 47/3 sccm oxygen/fluoroform at 300 W the undercut ratios were measured to be 1.0 and 0.5 at 300 and 100 mTorr respectively. These undercut ratios were measured before the full thickness of the polymer was etched. Equal vertical (Y) and horizontal (X) etch depths at 300 mTorr indicate that the etching process was isotropic. At a lower pressure, the concentration of oxygen decreased and the ionic bombardment increased, reducing the undercut ratio. In addition, reducing the fluoroform will also reduce the undercut ratio. However, less fluoro-l form also lowers the etch rate. After the full thickness of the film has been etched, the horizontal etch rate generally increases by a factor of two to three.

To achieve anisotropic etching, it is necessary to reduce the oxygen and fluorine concentrations in the plasma while





Fig. 9. SEM observation of BPNB-10 surfaces after etching under 47/3 sccm oxygen/fluoroform at 300 W and (a, top) 50 mTorr or (b, bottom) 300 mTorr. Dummy wafers are used to cover most area of the power electrode.

keeping ion bombardment high. To achieve this, an inert gas, argon, was added to the oxygen/fluoroform mixture. Argon can be ionized in the plasma and provides mostly ion bombardment without chemical attack. For a total gas flow of 50 secm, 40 secm of argon was found to provide significant improvement in the anisotropy. Etch depth curves for polynorbornene as a function of oxygen/fluoroform/argon mixtures are shown in Fig. 11. The etching conditions for the experiments were 50 sccm total flow rate, 300 W rf power and 300 mTorr pressure for a total time of 2 min. Note that the etch rate of polynorbornene does not decrease substantially using 10/40 oxygen/argon instead of 50 sccm pure oxygen. This is because the rate-limiting step in the etching process is the removal of the silicon dioxide in the fluorinefree process. The addition of fluoroform at low concentrations (1.5 sccm) or 3% by volume) increases the etch rate. At a higher fluoroform flow rate, the etch rate decreased. At a

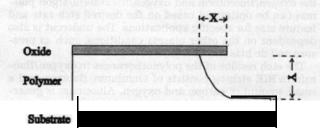


Fig. 10. Typical cross-sectional view under SEM for patterned pofynorbornenes after RIE.

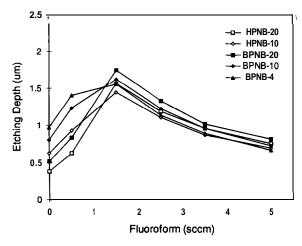


Fig. 11. Etch depth for polynorbornenes as a function of oxygen/ fluoroform/argon mixture composition. Etching conditions: (10-x)/ x/40 sccm oxygen/fluoroform/argon, 300 mTorr, 300 W, and 2 min.

low fluoroform flow rate, the etch rate order was BPNB-4 >BPNB-10 >HPNB-10 >BPNB-20 >HPNB-20. This order indicates that the amount of fluorine is insufficient to remove the silicon oxide formed on the etched surface. When the fluoroform flow rate was more than 1.5 sccm, the etch rate order switches to BPNB-20 >BPNB-10 >HPNB-20 >BPNB-4 >HPNB-10, just as it is in the oxygen/fluoroform plasma. Unlike the oxygen/fluoroform etching system, the etch rate does not continue to increase up to a fluoroform flow rate of 3 to 5 sccm, because there is too little oxygen.

For BPNB-4 etched in 8.5/1.5/40 sccm oxygen/fluoroform/argon at 300 W RF power and 300 mTorr pressure, the etch undercut ratio was measured to be 0.36. This value is much lower than the value obtained in the 47/3 sccm oxygen/fluoroform plasma (1.0) keeping all other plasma conditions the same. This value is also significantly less than the undercut ratio of 0.5 obtained at 100 mTorr and 300 W in the 47/3 sccm oxygen/fluoroform plasma. This result indicates that higher anisotropy can be achieved with the addition of argon. Additional evidence is provided by the fiberlike residue formed at 300 mTorr etching in the 8.5/1.5/40 sccm oxygen/fluoroform/argon plasma, which is not seen at 300 mTorr etching in the oxygen/fluoroform plasma. As discussed in the last section, the fiberlike residue suggests that the vertical etching is not able to etch the polymer under the aluminum-based residue, thus the fiberlike residue is formed.

#### Conclusion

The RIE of polynorbornenes in an oxygen plasma results in a porous surface layer containing mainly silicon dioxide. The etch rate is dependent on the silicon content of the polymers. The addition of a small amount of fluoroform effectively removes the silicon oxide and increases the etch rate of the polynorbornenes. However, fluoroform also produces significant undercut due to its isotropic chemical etching. To alleviate the undercut, oxygen/fluoroform was diluted with argon gas, thus increasing the ion bombardment and anisotropy. The amount of fluoroform needed in the oxygen/fluoroform and oxygen/fluoroform/argon plasmas can be optimized based on the desired etch rate and feature size for specific applications. The undercut is also dependent on the other plasma conditions, such as pressure and dc bias.

The etch residue of the polynorbornenes in oxygen/fluoroform RIE etching consists of aluminum, fluorine, and a small amount of carbon and oxygen. Aluminum is gener-

ally a contaminant from the back sputtering of the powered electrode. The shape of etch residue is dependent upon the plasma conditions. At the higher pressure, isotropic chemical etching produced an islandlike residue. In contrast, a fiberlike residue was formed at lower pressures. Postetch treatments, such as rinsing with acidic solutions, have been shown to be effective cleaning methods.

### Acknowledgments

The authors would like to acknowledge BF Goodrich Company for providing polynorbornene materials and financial support for this study The support of the National Science Foundation Packaging Research Center at Georgia Institute of Technology is also gratefully acknowledged.

Manuscript submitted August 14, 1997; revised manuscript received November 24, 1997.

Georgia Institute of Technology assisted in meeting the publication costs of this article.

#### REFERENCES

- 1. H. B. Bakoglu, Circuits Interconnections and Packaging for VLSI, p 135, Addison-Wesley, Reading, MA
- 2. S. Takeishi, R. Kudoh, R. Shinohara, A. Tsukune, Y. Satoh, H. Mirazawa, H. Harada, and M. Yamada, J.

Electrochem. Soc., **143**, **381** (1996).
3. G. J. Dishon, S. M. Bobbio, T. G. Tessier, Y. S. Ho, and R. F. Jewett, *J. Electron. Mater.*, **18**, **293** (1989).

4. G. Messner, I. Turlik. J. Balde, and P. Garrou. Multichip Modules, P 122, ISHM, Reston, VA (1992).

S. Bothra, M. Kellam, and P. Garrou, J. Electron. Mater., 23, 8 (1994).
 R. Allen, R. Sooriyakumaran, J. Opitz, G. Wallraff, M.

- Gregory, R. DiPietro, B. Breyta, D. Hofer, R. Junz, S. Jayaraman, R. Shick, B. Goodall, U. Okoroanyanwu, and G. Wilson, in *SPIE Proc.*, **XIII.** 2724 (1996). S P I E - I n t . Soc. Opt. E n g . 7. R. Allen, J. Opitz, C. Larson, T. Wallow, R. DiPietro, B. Breyta, R. Sooriyakumaran, and D. Hofer, *J. Photokykus* C. J. J. J. J. J. 202 (1997).
- topolym. Sci. Technol., 10, 503 (1997).
  B. L. Goodall, G. M. Benedikt, L. H. McIntosh, D. A. Barnes, and L. F. Rhodes, U.S. Pat. 5,468,819 (1993).
- 9. N. R. Grove, Q. Zhao, P. A. Kohl, S. A. Bidstrup, R. A. Shick, B. L. Goodall, L. H. McIntosh, and S. Jayara-
- man, Advancing Microelectronics, 23, 16 (1996).

  10. R. F. Heichelderfer, J. M. Welty, and J. F. Battey, J. Electrochem. Soc., 124, 1926 (1977).
- 11. M. A. Hartney, D. W. Hess, and D. S. Soane, *J. Vac. Sci. Technol.*, **B7**, 1 (1989).
- N. J. Chou, C. H. Tang, J. Paraszczak, and E. Babich, *Appl. Phys. Lett.*, 46, 31 (1985).
   F. Watanabe and Y. Ohnishi, J. Vac. Sci. Technol., B4,
- **422** (1986).
- 14. C. W. Jurgensen and A. Rammelsberg, J. Vac. Sci. Technol., A7, 3317 (1989). 15. J. Dijkstra, H. Kalter, and G. ven de Ven, *Microelec*-
- tron. Eng., 13, 455 (1991). 16. 0. Joubert and M. Pons, J. Vac. Sci. Technol., B11, 1
- (1993).17. J. Dijkstra, J. Vac. Sci. Technol., **B10**, 2222 (1992).
- 18. Y. L. Ysang, C. Miller, and T. Lii, J. Electrochem. Soc., 143, 1464 (1996).
- 19. Y. T. Lii and J. T. Wetzel, in ULSI Science and Technology, E. M. Middlesworth and H. Massoud, Editors, PV 95-5, p 266, The Electrochemical Society Pro-

ceedings Series, Pennington, NJ (1995). 20. R. D. Tacito and C. Steinbruchel, *J. Electrochem. Soc.*, 143, 2695 (1996).

21. N. R. Grove, P. A. Kohl, and S. A. Bidstrup-Allen, J.

Polym. Sci., Part B: Polym. Phys., Submitted. 22. G. S. Oehrlem, J. G. Clabes, and P. Spirito, J. Electrochem. Soc., 133, 1002 (1986).

- 23. G. S. Oehrlein, G. J. Scilla, and S. J. Jeng, Appl. Phys.
- Lett., 52, 907 (1988). 24. J. P. Simko, G. S. Oehrlein, and T. M. Mayer, *J. Elec*trochem. Soc., 138, 277 (1991).