Evaluation of Halogenated Polyimide Etching for Optical Waveguide Fabrication by Using Inductively Coupled Plasma

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ABSTRACT: Oxygen plasma etching of a series of halogenated polyimides was carried out for low-loss waveguide fabrication by using inductively coupled plasma (ICP). The effects of etching parameters such as ICP power, rf power, and O_2 flow rate on the etching rate and etching profile of polymer films were investigated. The increase in the etch rate with the ICP power and the rf power was observed. Both the vertical profile and sidewall roughness were found to be related to the ion energy (dc bias). By optimizing these parameters, a vertical profile and a smooth sidewall were obtained by 500 W of ICP power, 150 W of rf power, 5 mTorr of chamber pressure, and 40 sccm of the O_2 flow rate. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 176–182, 2001

Key words: plasma etching; halogenated polyimides; low scattering loss; optical waveguides; inductively coupled plasma

INTRODUCTION

Fluorinated or chlorinated polyimides are expected to be used as light-transmitting media in the optical communication wavelengths region for optoelectronic integrated circuits (OEICs) and optical multichip modules (MCMs), due to their low optical loss and refractive controllability together with excellent thermal and chemical stability.[1–5] Polymer optical waveguide fabrication adopts the standard semiconductor processing technology such as spin-coating, baking, and etching processes. Among the etching methods for fabrication of polymeric waveguides, plasma etching is one of the most advanced fabrication methods. In this method, the polymer outside the waveguide channel is removed by reactive ions—typically, oxygen ions. It is known that the plasma-etching mechanism is physicochemical, where both isotropic etching by chemical attack and anisotropic etching by ionic bombardment take place.[6] Efforts have been made for the optimization of the waveguide fabrication process, in particular, deep, smooth, and vertical sidewall etching to minimize optical losses due to the sidewall scattering.[7,8] Low optical loss is one of the critical considerations for waveguides. Besides optical loss from intrinsic material-absorption losses, scattering losses from the roughness of the etched surfaces after the etching process is a major source of optical loss. Therefore, smooth surfaces should be obtained to reduce the optical loss of waveguides.

Conventional reactive ion etching (RIE) has been widely used in optical waveguide fabrication.[9,10] In RIE, only one rf power is applied to regulate both plasma density and ion energy (or dc bias) and it is impossible to control them sep-

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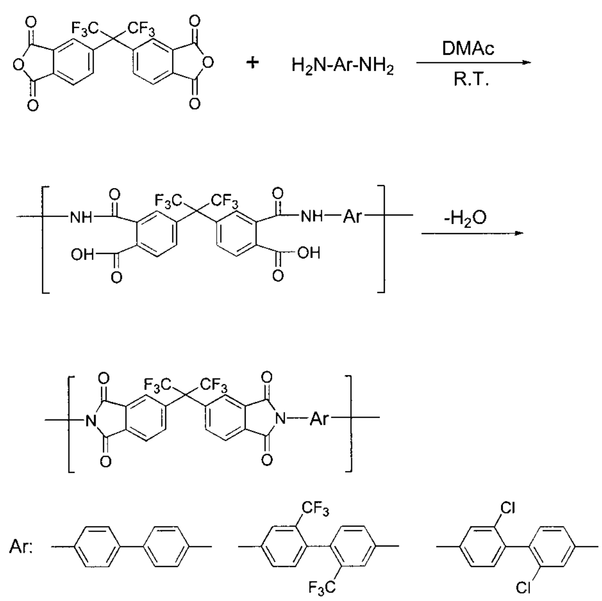
arately. Although the etch rate increases with the rf power, the increased rf power can cause severe sputtering of ions at the sample surface, leading to increased damage on the sample. In this regard, high-density plasma etching using an inductively coupled plasma (ICP) source offers an attractive alternative over the conventional RIE.[11,12] ICP etching uses ICP power to generate high-density plasma (typically two to three orders of magnitude larger than that for RIE) without being correlated to the ion energy. Thus, ICP etching may produce low surface damage while achieving high etch rates. In this article, systematic ICP etching of a series of halogenated polyimides films was conducted to characterize the etching behavior of these polyimides. The etch rate, vertical profile, and sidewall roughness of the channel waveguide were studied as a function of the ICP power, the rf power (dc bias), and the O_2 flow rate. The effect of the halogen moiety (Cl and F) in the polymers on the etching properties was also investigated.

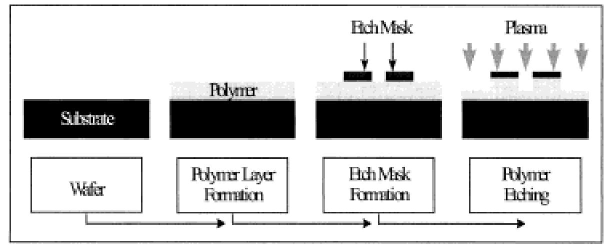
EXPERIMENTAL

Materials

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, Chriskev, Leawood, KS) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB, Fluoro Chemicals, Derbyshire, UK) were



Scheme 1



Scheme 2

dried at 150°C under reduced pressure and sublimated prior to use. 4,4′-Diaminobiphenyl (DABP) and 2,2′-dichloro-4,4′-diaminobiphenyl (DCB) were prepared according to the reported procedure.[13,14] *N*,*N*′-Dimethylacetamide (DMAc, Aldrich, Milwaukee, WI) was purified by distillation under reduced pressure over calcium hydride.

Polymerization and Film Preparation

Chlorine- and fluorine-containing polyimides were prepared according to the general reaction shown in Scheme 1. Polymerizations were carried out under a nitrogen atmosphere by adding a stoichiometric amount of diamine and dianhydride in DMAc at room temperature. The resulting poly(amic acid) solutions were filtered through a 0.2-μm Teflon filter and then spun-coated onto a silicon wafer, followed by curing at 80°C/2 h, 160°C/1 h, 250°C/0.5 h, 300°C/0.5 h, and 350°C/0.5 h. The thickness of the films was about 15 μm.

Plasma Etching

A 100-nm-thick SiO_2 layer was sputtered onto the top of the polyimide films as an etch mask layer for the subsequent etching of the polyimide. To define the waveguide patterns on the SiO_2 layer,

Table I Thermal Properties of the Polyimides

Polymer	T_g (°C)[a]	Onset Temperature of Weight Loss[b]
6FDA/DABP	362	530
6FDA/PFMB	350	515
6FDA/DCB	354	512

[a] Determined by DSC at a heating rate of 20°C/min in a nitrogen atmosphere.
[b] Determined by TGA at a heating rate of 10°C/min in a nitrogen atmosphere.

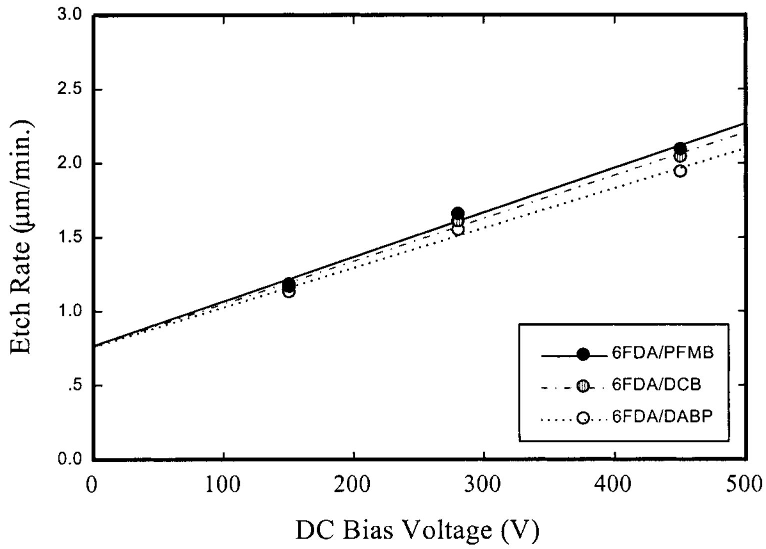


Figure 1 Etch rates as a function of rf (dc bias) at 500 W ICP power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate.

AZ 6112 photoresist (Hoechst, Frankfurt, Germany) was spin-coated onto the SiO_2 layer and patterned using a conventional photolithography technique. The SiO_2 mask layer was etched using an ICP system in a CF_4 plasma with the developed photoresist as an etch mask. ICP etching of polyimide films in O_2 plasma with the SiO_2 mask was performed under various conditions. The etching conditions were varied by changing the parameters: ICP power (200–800 W), rf power (65–315 W), and oxygen flow rate (5–40 sccm). Argon (Ar) plasma etching of the polymer films was also conducted for comparison. This process is illustrated in Scheme 2.

Measurements

The glass transition temperatures (T_g) of the polymers were measured on a Perkin–Elmer DSC7 at a heating rate of 20°C/min in a nitrogen atmosphere. Thermogravimetric analysis was performed on a DuPont TGA 2950 thermal analyzer at a heating rate of 10°C/min in a nitrogen atmosphere. The inherent viscosities of the poly(amic acid) samples were measured with an Ubbelodhe viscometer using *N*-methyl-2-pyrrolidinone (NMP) as a solvent. The etch depth was measured by a surface profiler. Both etch profiles and surface morphologies were characterized by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Preparation of Polymers and Their Thermal Properties

Chlorofluorinated and fluorinated polyimides were synthesized from 6FDA with DCB, PFMB, and DABP. The intrinsic viscosities of the resulting poly(amic acid)s were between 1.8 and 2.2 dL/g, measured at 30°C in NMP, illustrating the high molecular weights of these polymers. The glass transition temperatures (T_g) and onset temperatures of the weight loss of the polyimides are summarized in Table I. The resulting polymers have T_g values around 350°C and show no appreciable weight loss up to 515°C in the TGA thermograms, indicating good thermal stability.

Table II Etch Rates of Polyimides as a Function of rf Power (dc Bias) at 500 W ICP Power, 5 mTorr Chamber Pressure, and 40 sccm O_2 Flow Rate

	Material			
Parameter	6FDA/ PFMB	6FDA/ DCB	6FDA/ DABP	Dc Bias Voltage (V)
Etch rate (μm/min)	1.19	1.17	1.13	150
	1.66	1.61	1.55	280
	2.10	2.05	1.95	450

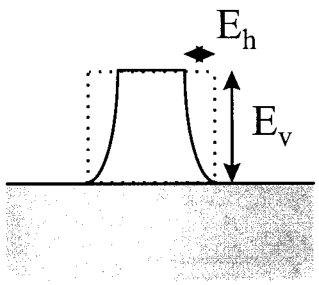


Figure 2 Anisotropy of etch profile; $A = 1 - (E_h/E_v)$, where E_h is the horizontal etch depth and E_v is the vertical etch depth.

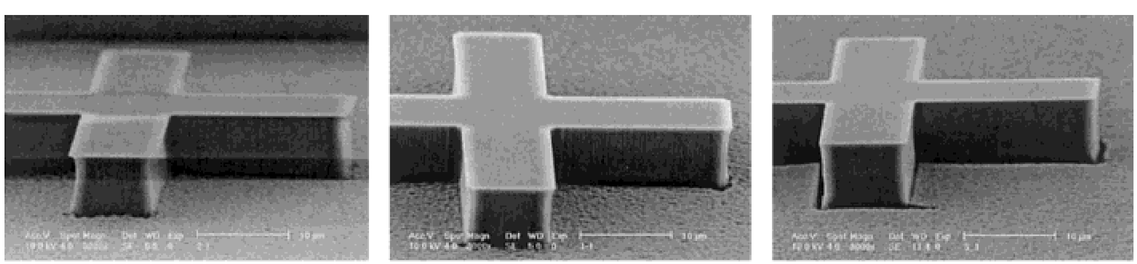
Plasma Etching

Effect of rf Power

The effect of rf power (dc bias) on the etch rates of the polyimides was investigated. The rf power was varied from 65 (150 V dc bias) to 315 W (450 V dc bias) while other parameters were fixed at 500 W ICP power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate. Figure 1 shows the effect of the rf power on the etch rates of the polyimides. As shown in Figure 1, etch rates of the samples were increased as the rf power was increased. Under the fixed ICP power condition (same plasma density), the physical etching by ion bombardment increases with the rf power (dc bias). Etch rates of polyimides at different rf power are summarized in Table II. Although the etch rates seem to be increased in the order of 6FDA/PFMB > 6FDA/DCB > 6FDA/DABP, it can generally be said that there are no dramatic differences in the etch rates among the polymers at each rf power condition. It seems that the effect of the halogen moiety in the polymer on the etch rate is negligible. The etch rate per dc bias (etch rate/dc bias) was calculated for each polyimide and is between 0.00268 and 0.00300 μm/min V. The etch profile was observed by SEM analysis.

The anisotropy of the etch profile was determined by $A = 1 - (E_h/E_v)$,[15] where E_h is the horizontal etch depth and E_v is the vertical etch depth as shown in Figure 2. The large value of anisotropy means a more vertical profile. The anisotropy was increased with the rf power. The anisotropy value of 6FDA/PFMB increased from 0.83 to 0.96 as the rf power was increased from 65 to 315 W.

It is generally known that reactive ion etching is a combination of two etching process—isotropic etching by chemical reaction between reactive ions and a substrate and anisotropic etching by ionic bombardment. In ICP etching processes, ICP power is the main factor that controls the plasma density and the rf power (dc bias) varies the ion-bombarding energy. Under the same plasma density (ICP power) condition, the ion-bombarding energy increases with the rf power. This increased ion-bombarding energy gives more directionality to the ion and, consequently, better anisotropy. Under the low rf power conditions, the etch profiles have a severe undercut as shown in Figure 3(a). Under this condition, the contribution of isotropic etching by chemical reaction is larger than that of anisotropic etching by ion bombardment due to the lower energy of the ion and directionality. When high rf power was applied, the ion bombardment was more predominant. This resulted in good anisotropy as shown in Figure 3(c). Although the etching rate and aniosotropy were increased as the rf power increased, a bottom trench or crack was observed at



(a) (b) (c)

Figure 3 Etch profiles of 6FDA/PFMB for different rf conditions at 500 W ICP power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate: (a) low rf (65 W) condition, $A = 0.83$; (b) middle rf (150 W) condition, $A = 0.89$; (c) high rf (315 W) condition, $A = 0.96$.

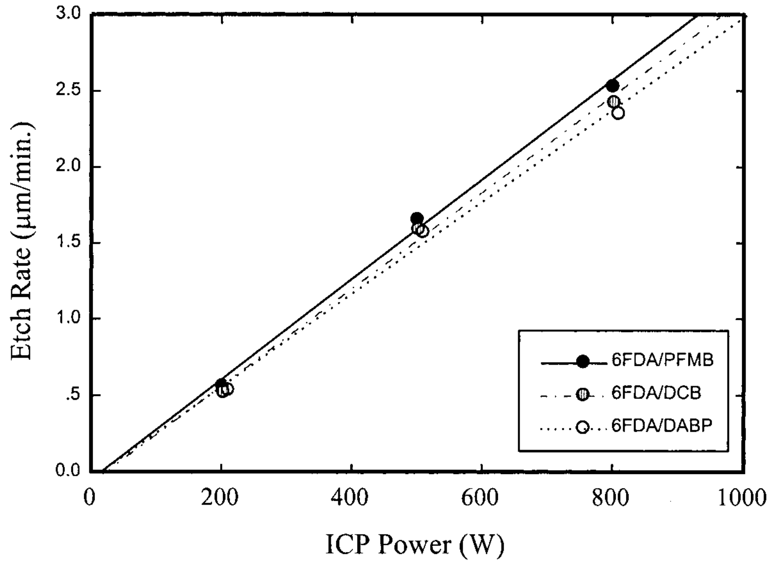


Figure 4 Etch rates as a function of ICP power at 150 W rf power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate.

higher rf power due to high ion-energy bombardment.

Effect of ICP Power

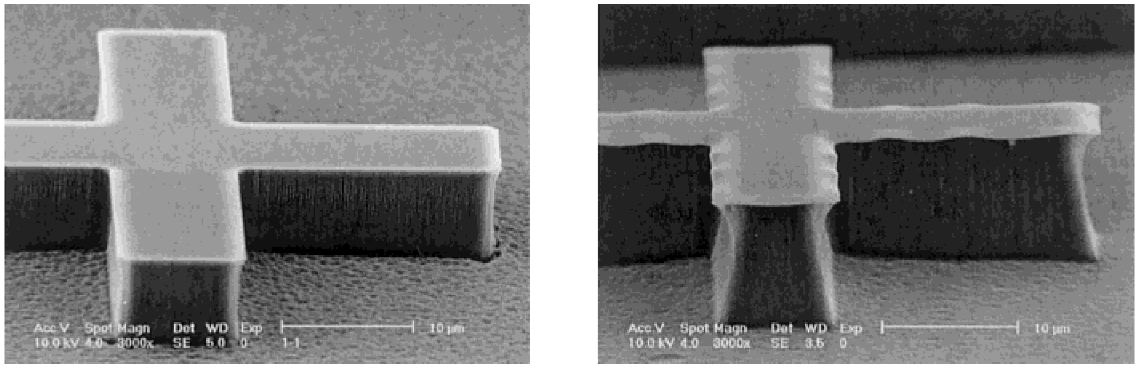
ICP etching of the polyimides was carried out with varying the ICP power while other parameters were fixed at 150 W rf power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate. Figure 4 shows the effect of the ICP power on the etch rate of the polyimides. As shown in this figure, increases in the etch rate were observed in all samples as the ICP power increased from 200 to 800 W. These results are summarized in Table III. The ratio of the etch rate to the ICP power (etch rate/ICP power) was calculated for each polyimide and is between 0.00300 and 0.00328 μm/min W. This value is larger than is the rate for the dc bias. This result indicates that the etch rate is more sensitive to the ICP power than to the dc bias based on our experimental conditions. Figure 5 shows the etch profile of 6FDA/PFMB observed by SEM at two different ICP power levels: 500 and 800 W. Although an increased etch rate was observed at 800 W ICP power, severe undercuts were observed at this ICP power. It is known that ICP power is responsible for dissociation of gas molecules into reactive ionic species, thus increasing the plasma density. The increase in the etch rate is attributed to the increased reactive species generated by the ICP power under a fixed rf power condition. Therefore, isotropic chemical etching is more dominant as the ICP power increases. This results, however, in poor anisotropy and rough side walls. Although poor anisotropy was observed at a high ICP power condition, formation of the trench or crack which was observed at a high rf condition [see Fig. 3(c)] was not observed. These results indicate that a moderate ion energy (150 W of rf power) and ICP power (500 W) are required to achieve a vertical profile and smooth sidewalls and to prevent trench or crack formation.

Table III Etch Rates of Polyimides as a Function of ICP Power at 150 W rf Power, 5 mTorr Chamber Pressure, and 40 sccm O_2 Flow Rate

	Material			
Parameter	6FDA/ PFMB	6FDA/ DCB	6FDA/ DABP	ICP Power (W)
Etch rate (μm/min)	0.57	0.54	0.52	200
	1.66	1.61	1.55	500
	2.53	2.45	2.33	800

Effect of O_2 Flow Rate

The effect of the O_2 flow rate on the etch rate of polyimides was investigated. The O_2 flow rate was varied from 5 to 40 sccm at 5 mTorr chamber



(a) (b)

Figure 5 Etch profiles with varying ICP power at 150 W rf power, 5 mTorr, and 40 sccm O_2: (a) 500 W ICP power condition; (b) 800 W ICP power condition.

pressure, 500 W ICP power, and 150 W rf power. Figure 6 shows the effect of the O_2 flow rate on the etch rate. The etch rate increased linearly as the O_2 flow rate increased from 5 to 20 sccm. However, further increases in the O_2 flow rate from 20 to 40 sccm did not change the etch rate appreciably. It seems that as the O_2 flow rate is increased the reactive ion species increases under the given conditions and this increased ion density results in an increment change in the etch rate. Around 20 sccm of the O_2 flow rate, the ion density is saturated, and the effect of this on the etch rate becomes less significant.

Effect of Argon

The effect of argon as a plasma source on the etching characteristics of a polymer (6FDA/PFMB) was investigated at 500 W ICP power, 150 W RF power, 5 mTorr chamber pressure, and 40 sccm Ar flow rate. These results are compared with those of oxygen plasma etching of a polymer at the same conditions. It is expected that the lower etching rate observed when using argon as a plasma source is because argon is a chemically inert gas and, subsequently, etching of the polymer is carried out only by ion bombardment. As expected, the etching rate obtained with oxygen is about 10 times higher than that measured with argon under the same conditions, which corresponds to 1.66 and 0.17 μm/min for oxygen and argon, respectively. These results confirm that the etching of polymers should be carried out in reactive plasma such as oxygen, in which the removal of the substrate is accelerated by a reac-

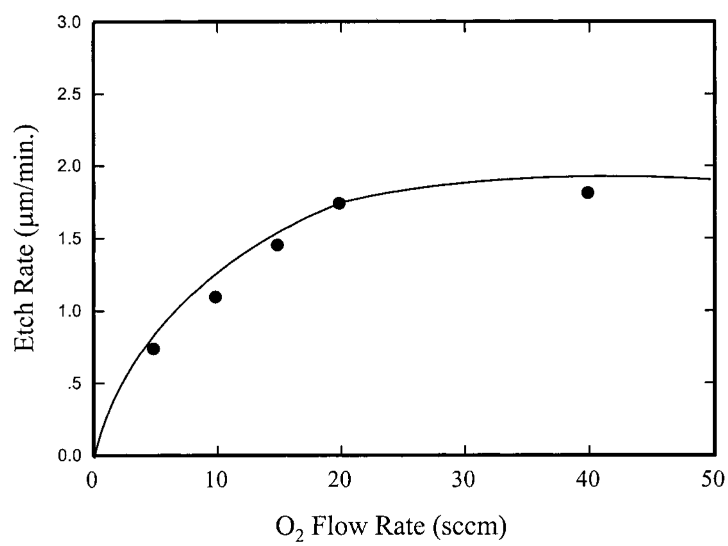
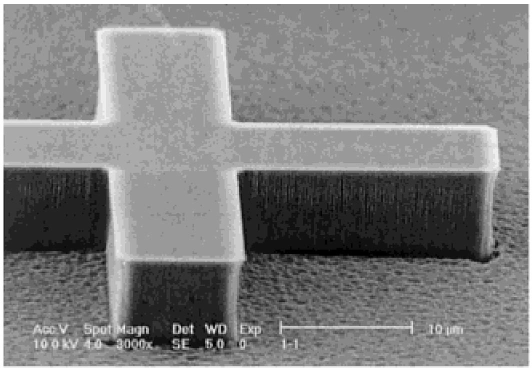
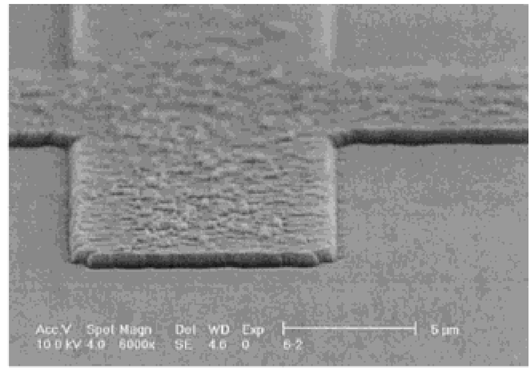


Figure 6 Etch rates as a function of O_2 flow rate at 500 W ICP power, 150 W RF power, and 5 mTorr chamber pressure.



(a)



(b)

Figure 7 Etch profiles at 500 W ICP power, 150 W rf power, 5 mTorr chamber pressure, and 40 sccm gas flow rate: (a) oxygen plasma; (b) argon plasma.

tion between the reactive species and the substrate atoms. The etching profile of a polymer with argon plasma was analyzed and this result was also compared with that of oxygen plasma etching. As shown in Figure 7, very rough top surfaces and low etch depths were observed when using argon gas as a plasma source.

CONCLUSIONS

The main advantage of ICP etching is to achieve high etch rates without damaging sample surfaces by essentially decoupling the plasma density and ion energy. ICP power controls the plasma density, whereas rf power controls the ion energy. The increase in the etch rate of the halogenated polyimides with ICP and rf power was attributed to an increased concentration of reactive species and increased ion bombardment, respectively. Both the vertical profile and sidewall roughness were found to be related to the ion energy. A moderate dc bias was required to achieve vertical profiles and smooth sidewalls, whereas a low dc bias was beneficial for reducing surface damage. Etch rates of 1.55–1.66 μm/min with a vertical profile and a smooth sidewall were obtained by ICP etching at 500 W ICP power, 150 W rf power, 5 mTorr chamber pressure, and 40 sccm O_2 flow rate. The effect of the halogen moiety (Cl and F) in the polymers on etch rate of the halogenated polyimides was found to be small.

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