

## ECR 식각 공정에 따른 층간절연막 폴리이미드의 전기적 특성

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### Electrical Properties of Interlayer Low Dielectric Polyimide with Electron Cyclotron Resonance Etching Process

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**Abstract :** The electrical properties of polyimide for interlayer dielectric applications are investigated with ECR (Electron Cyclotron Resonance) etching process. ECR etching with  $\text{Cl}_2$ -based plasma, generally used for aluminum etching, results in an increase in the dielectric constant of polyimide, while  $\text{SF}_6$  plasma exhibits a high polyimide etch rate and a reducing effect of the dielectric constant. The leakage current of the polyimide is significantly suppressed after plasma exposure. Combination of Al etching with  $\text{Cl}_2$  plasma and polyimide etching with  $\text{SF}_6$  plasma is expected as a good tool for realizing the multilevel metallization structures.

**초 록:** ECR (Electron Cyclotron Resonance) 식각 공정에 따른 층간 절연막 폴리이미드의 전기적 특성에 관하여 연구하였다. 알루미늄 식각시 일반적으로 사용되는  $\text{Cl}_2$  플라즈마는 폴리이미드의 유전상수 값을 증가시킨 반면에  $\text{SF}_6$  플라즈마의 경우는 높은 식각률과 유전상수 값의 감소를 가져왔다. 폴리이미드의 누설 전류는 ECR 식각 공정 후에 감소되었다. 다중 금속화 구조를 구현하는데 있어  $\text{Cl}_2$  플라즈마를 사용하여 알루미늄을 식각하고  $\text{SF}_6$  플라즈마를 사용하여 폴리이미드를 식각하는 것이 최적일 것으로 판단된다.

### 1. Introduction

As the size of features in integrated circuitry (IC) chips is scaled down, devices require interlayer dielectrics (ILDs) with low dielectric constant to reduce device resistance-capacitance (RC) delay, interconnect crosstalk, and power consumption.<sup>1</sup> Many types of polymers have been examined for use in ULSI devices.<sup>2-5</sup> Among them, polyimides are promising due to their high thermal stability and low dielectric constant that make them suitable for use as ILD in hybrid circuits and multichip modules (MCMs).

Plasma processes are indispensable for fabricating integrated circuits and devices. During Cl-based plasma etching of aluminum on ILD polyimides, the polyimides are subjected to plasma exposure. Polyimide damage is expected due to overetching during Cl-based plasma etching of aluminum on polyimides. Also, dielectric

etching has become an important issue in the realization of multi-level metallization structures. During the exposure of the polyimide to plasma, energetic particles (electrons, ions, photons, free radicals) interact with the organic surface via a process that involves heating, breaking of chemical bonds, crosslinking, reaction of surface free radicals and the formation of new chemical groups.

In this study, the electrical behavior of polyimide after exposure to various plasmas is investigated. Chemical composition and bonding of polyimide were characterized by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR).

### 2. Experimental

We used DuPont's experimental polyimide (PI 2610), which is a solution of biphenylene dianhydride-

phenylene diamine, BPDA-PDA. The solution was applied by spin coating on the  $\text{Al}(3000 \text{ \AA})/\text{SiO}_2(5000 \text{ \AA})/\text{Si}(100)$  structure. The spin speed was adjusted to have a film thickness of about  $1.5 \mu\text{m}$  after curing. In order to convert polyamic acid into polyimide, soft curing at  $135^\circ\text{C}$  for 30 minutes and hard curing at  $350^\circ\text{C}$  for 1 hour were performed. After this process, the polyimide film was exposed to various plasmas using an electron cyclotron resonance (ECR) downstream etcher with several gas chemistries ( $\text{SF}_6$ ,  $\text{Cl}_2$ ,  $\text{Cl}_2/\text{N}_2$ ,  $\text{Cl}_2/\text{O}_2$ ). The source power and bias power were fixed at 1000W and 150 W, respectively. A working pressure of 10 mTorr and a total flow rate of 15 sccm were maintained during plasma exposure. An Al upper electrode was deposited on the polyimide film and patterned by wet etching to measure the dielectric constant and leakage current of the polyimide. Dielectric properties of polyimides were analyzed using a HP4149A impedance analyzer at 1 MHz and leakage current was measured by HP4145B using Al/PI/Al capacitor structures. Chemical analyses were conducted using FTIR and XPS.

### 3. Results and Discussion

Fig. 1 shows the dielectric constant of the polyimide after exposure to  $\text{Cl}$ -based plasmas as a function of the exposure time. The dielectric constant of the polyimide increases with increasing the exposure time especially with the addition of  $\text{O}_2$  and  $\text{N}_2$ . This is attributed to the higher polarizability of  $\text{O}_2$  and  $\text{N}_2$ , which form bonds with polyimide during plasma treatment.<sup>6</sup> This result is undesirable because polyimide should have a low dielectric constant for ILD applications. We examined the effect of  $\text{SF}_6$  plasma with the aim to lower the

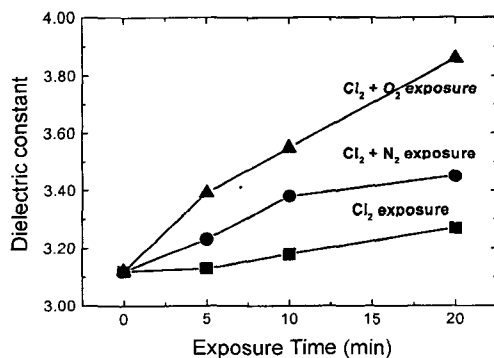


Fig. 1. Variation of the dielectric constant of the polyimide after exposure to  $\text{Cl}$ -based plasmas.

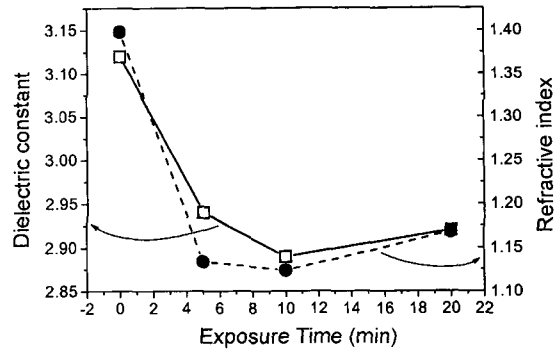


Fig. 2. Dielectric constant and refractive index of the polyimide as a function of the exposure time to  $\text{SF}_6$  plasma.

dielectric constant. It is well known that doping silicon dioxide with fluorine can reduce its dielectric constant. It was observed that both the dielectric constant and the refractive index of polyimide decrease with increasing the exposure time to  $\text{SF}_6$  plasma below 5 minutes exposure time and saturate above 5 minutes due to the reaction of fluorine with the surface of polyimide (Fig. 2). This phenomenon is due to the lower polarizability and molar refractivity of fluorine than that of other plasma species. This is consistent with the results of Maruo *et al.*<sup>7</sup> who found that synchrotron irradiation causing the desorption of fluorine from polyimide results in the increase in the dielectric constant and the refractive index.

Leakage current density of the polyimide exposed to various plasmas was measured at an electric field of  $1\text{MV}/\text{cm}$  (Fig. 3). The leakage current density of the polyimide exposed to various plasmas ( $2.68 \times 10^{-10}$ – $3 \times 10^{-9} \text{ A}/\text{cm}^2$ ) is three or four orders of magnitude lower than that of as-cured polyimide ( $1.46 \times 10^{-6} \text{ A}/\text{cm}^2$ ), and is comparable to that of silicon dioxide.<sup>8</sup> It is inferred that plasma exposure assists in the surface modification of polyimide and the formation of interfacial bonds between aluminum and polyimide<sup>9</sup> because interface trap density due to the incoherent bonding between polyimide and aluminum causes the leakage current to increase.

In order to determine the reason behind the observed dielectric behaviors, chemical bonds were examined using FTIR (Fig. 4). In the polyimide exposed to  $\text{SF}_6$  plasma, the absorption band at  $730\text{--}745 \text{ cm}^{-1}$  assigned to  $-\text{CF}_2-\text{CF}_3$  deformation which breaks the aromatic ring and that at  $950\text{--}1100 \text{ cm}^{-1}$  assigned to polyfluorinated benzene compound without opening breakage of the

Various plasma	Leakage current density
As cured	$1.466 \times 10^{-6}$
Cl <sub>2</sub>	$4.669 \times 10^{-10}$
Cl <sub>2</sub> +N <sub>2</sub>	$7.160 \times 10^{-10}$
Cl <sub>2</sub> +O <sub>2</sub>	$3.575 \times 10^{-9}$
SF <sub>6</sub>	$2.68 \times 10^{-10}$

Fig. 3. Leakage current density of the polyimides after exposure to various plasmas.

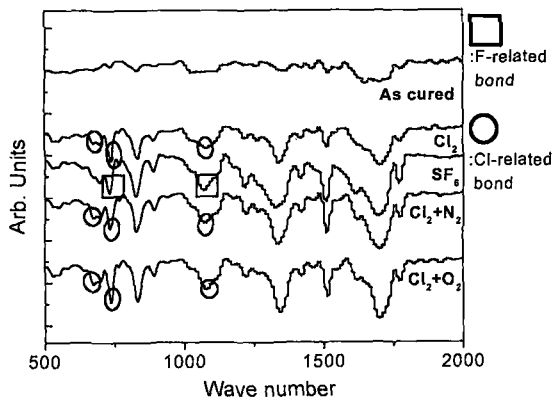


Fig. 4. Infrared spectra of the polyimides exposed to various plasmas.

aromatic ring, were found.<sup>10</sup> Similar results were observed in polyimides exposed to Cl-based plasma, where increases in the intensity of the absorption bands at 1083, 739 and 685 cm<sup>-1</sup> were observed. These bonds can be assigned to chlorobenzene compounds. It is possible that the formation of these halogenide caused bond scission through the abstraction of hydrogen from the benzene ring,<sup>11</sup> resulting in decreasing the dielectric constant according to the Clausius-Mossotti relation.<sup>12</sup> However, there is another factor affecting the dielectric constant, which is molar refractivity. Dielectric constant ( $\epsilon$ ) is related to polarizability ( $\alpha$ ), which, in turn, is also proportional to molar refractivity ( $n$ ). This results in the relationship between dielectric constant and molar refractivity of  $n^2 \approx \epsilon$ .<sup>12</sup> Molar refractivity of chlorine is about 9.0 while those of fluorine, carbon, and hydrogen are 0.81, 2.59 and 1.03, respectively.<sup>6</sup> As a result, chlorine incorporation increases the dielectric constant, while fluorine decreases it. We observed that intensities of cyclic imide C-N stretching at 1340-1360 cm<sup>-1</sup> and carbonyl C=O stretching at 1700 cm<sup>-1</sup>,<sup>10,13</sup> increased with Cl<sub>2</sub>/N<sub>2</sub> and Cl<sub>2</sub>/O<sub>2</sub> plasma treatments, respectively. The high polarity of the newly incorporated N<sub>2</sub> or O<sub>2</sub> is

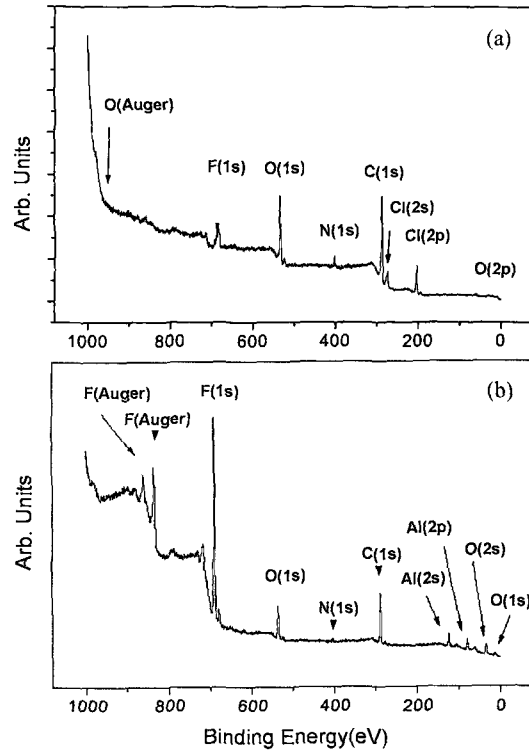


Fig. 5. XPS spectrum of the polyimide exposed to Cl<sub>2</sub> and SF<sub>6</sub> plasmas. Wide scanning showing (a) chlorine incorporation and (b) fluorine incorporation.

speculated to increase the dielectric constant of the polyimide. When the surface of as-cured polyimide is exposed to Cl<sub>2</sub>/O<sub>2</sub> plasma, the imide ring in the polyimide is opened to form additional C-O and C-OH bonds. As the number of C-OH bonds increases, a hydrophilic surface is also created by Cl<sub>2</sub>/O<sub>2</sub> plasma, which can cause the increase of the dielectric constant of the polyimide.<sup>14</sup>

XPS analysis was conducted to investigate the chemical configuration of the polyimide more closely. The XPS spectra in Figs. 5(a) and (b) show a considerable incorporation of C<sub>1</sub> and F into the polyimide after Cl<sub>2</sub> and SF<sub>6</sub> plasma treatments, respectively. To observe the chemical configuration, C 1s spectra were analyzed, and the results are shown in Fig. 6. A significant shift of C 1s peaks to the higher binding energy region is observed after plasma treatment, which implies bond formation with higher electronegative species. The deconvoluted spectra of Cl<sub>2</sub>-plasma-treated polyimide in Fig. 6(a) shows a peak at 286.6 eV which is possibly due to C-C, C-H or C-N

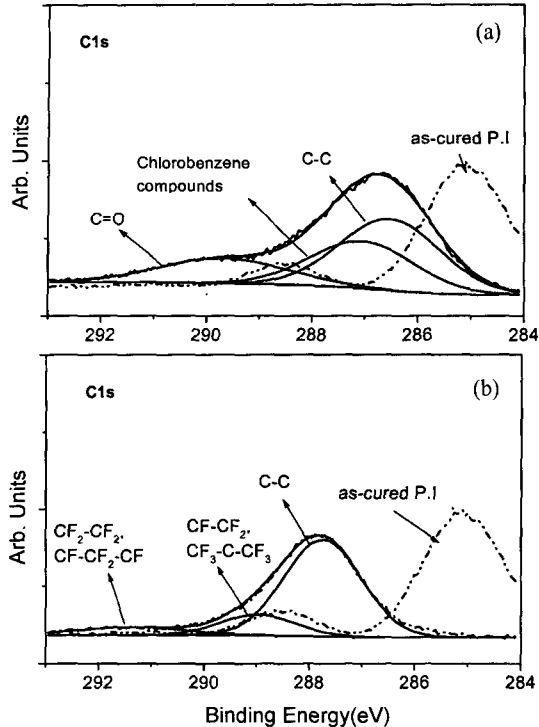


Fig. 6. XPS spectrum of C 1s and deconvoluted spectra. (a) polyimide and polyimide exposed to  $\text{Cl}_2$  plasma, (b) polyimide and polyimide exposed to  $\text{SF}_6$  plasma.

bonds. The second feature at 287.1 eV indicates the existence of chlorobenzene, and the highest binding energy feature at 289.7 eV is assumed to be from carbonyl carbon.<sup>13,15</sup> Figure 6(b) for  $\text{SF}_6$ -plasma-treated polyimide shows a peak at 287.8 eV which is attributed to the emission from C-C, C-N, or C-O bonds. The feature at 289 eV is probably due to  $\text{CF-CF}_2$ ,  $\text{CF}_3\text{-C-CF}_3$ ,  $\text{-CF-CF-CF-}$ , and the highest binding energy at 291.4 eV is likely due to  $\text{CF}_2\text{-CF}$ ,  $\text{CF}_2\text{-CF}_2$ ,  $\text{CF-CF}_2\text{-CF}$  or  $\text{-CF}_2\text{-CF}_2\text{-CF}_2\text{-}$ .<sup>13,15</sup>

Even though  $\text{SF}_6$  plasma cannot be used for Al etching due to the formation of nonvolatile etch products,<sup>16</sup> it is effective in terms of decreasing the dielectric constant of the polyimide. In addition,  $\text{SF}_6$  plasma shows a significantly higher polyimide etch rate than  $\text{Cl}_2$  plasma (Fig. 7). This is useful in the etching of polyimide. The optimal combination of these two plasma processes will be a good tool in realizing multilevel metallization structures utilizing polyimide as the ILD layer.

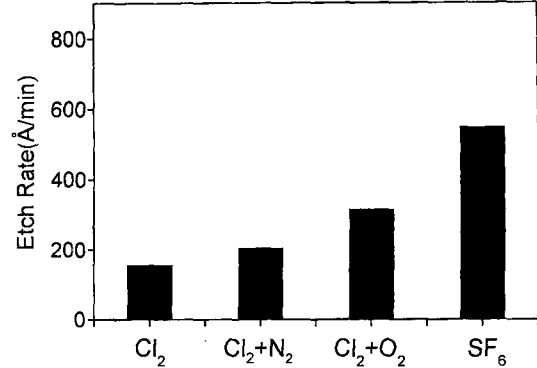


Fig. 7. Etch rate of polyimide with various ECR plasmas.

#### 4. Conclusions

We investigated the properties of polyimides exposed to various plasmas, and reached the following conclusions.

(1) ECR etching of the polyimide with the Cl-based plasmas which are usually used for Al etching, caused the problem of increasing the dielectric constant of the polyimide.

(2) The dielectric constant of the polyimide was effectively reduced by exposure to  $\text{SF}_6$  plasma.

(3) The leakage current density of the polyimide was decreased after plasma exposure to Cl-based plasmas as well as  $\text{SF}_6$  plasma.

(4) FTIR and XPS studies implied that Chlorine and fluorine atoms form chemical bonds with the polyimide.

(5) The etch rate of polyimide is much higher with  $\text{SF}_6$  plasma than with  $\text{Cl}_2$  plasma.

(6) Multilevel metallization could be performed by optimized plasma process with  $\text{Cl}_2$  in combination with  $\text{SF}_6$ .

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