Proc. 5th Int. Joint Symp. on Microelec. and Packaging,
IMAPS-Korea and IEEE-CPMT, Seoul, Korea, 2000.

Properties of Interlayer Low Dielectric Polyimide during Aluminum Etching with Electron Cyclotron Resonance Etcher System

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Abstract

The properties of polyimide for interlayer dielectric applications are investigated during plasma etching of aluminum on it. Chlorine-based plasma generally used for aluminum etching results in an increase in the dielectric constant of polyimide, while SF_6 plasma exhibits a high polyimide etch rate and a reducing effect of the dielectric constant. The leakage current of polyimide is significantly suppressed after plasma exposure. An optimal combination of Al etch with Cl_2 plasma and polyimide etch with SF_6 plasma is expected to be a good tool for realizing multilevel metallization structures.

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[1]. Many types of polymers have been examined for use in ULSI devices[2-5]. Among them, polyimide is promising due to its high thermal stability and low dielectric constant that make it suitable for use as an 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 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 finally the formation of new chemical groups.

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

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 Al(3000Å)/SiO_2(5000Å)/Si(100) structure. The spin speed was adjusted to give a film thickness of about 1.5㎛ after curing. In order to convert polyamic acid into polyimide, soft curing at 135℃ for 30 min and hard curing at 350℃ for 1 hr 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 (SF_6, Cl_2, Cl_2/N_2, Cl_2/O_2) The source power and bias power were fixed at 1000W and 150W, respectively. A working pressure of 10mTorr and a total flow rate of 15sccm were maintained during plasma exposure. An Al upper electrode was deposited on the polyimide film and patterned by wet etching for measurements of dielectric constant and leakage current. Dielectric properties of polyimides were analyzed using a HP4149A impedance analyzer at 1MHz 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

Figure 1 shows the behavior of the dielectric constant of polyimides during exposure to Cl-based plasma as a function of exposure time. The dielectric constant of polyimides increases with increasing exposure time especially with the addition of O_2 and N_2. This is attributed to the higher polarizability of O_2 and N_2, which form bonds with polyimide during plasma treatment[6)]. This result is undesirable because polyimide should have a low dielectric constant for ILD applications. We examined the effect of SF_6 plasma with the aim of lowering the 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 exposure time to SF_6 plasma (Fig. 2). This is consistent with the results of Maruo et al.[7)] who found that synchrotron irradiation causing the desorption of fluorine from polyimide results in the increase in the dielectric constant and the refractive index.

The leakage current density of polyimides exposed to various plasmas was measured at an electric field of 1MV/cm (Fig. 3). The leakage current density of polyimides exposed to various plasmas (2.68×10^{-10} - 3×10^{-9} A/cm^2) is three or four orders of magnitude lower than that of as-cured polyimide (1.46×10^{-6} A/cm^2), and is comparable to that of silicon dioxide[8)]. It is inferred that plasma exposure assists in the surface modification of polyimide and the formation of interfacial bonds between aluminum and polyimide[9)].

In order to determine the reason behind the observed dielectric behaviors, chemical bonds were examined using FTIR (Fig. 4). In the polyimide exposed to SF_6 plasma, the absorption band at 730~745cm^{-1} assigned to–

CF_2-CF_3 deformation which opens breaks the aromatic ring and that at 950~1100 cm^{-1} assigned to polyfluorinated benzene compound without opening breakage of the aromatic ring, were found [10]. Similar results were observed in polyimides exposed to Cl-based plasma, where increases in the intensity of the absorption bands at 1083,739 and 685cm^{-1} were observed. These bonds can be assigned to chlorobenzene compounds. It is possible that the formation of these halogenides results in bond scission through the abstraction of hydrogen from the benzene ring[11]. This will result in a decrease in the dielectric constant according to the Clausius-Mossotti relation[12]. However, there is another factor affecting the dielectric constant, which is molar refractivity. Dielectric constant (ε) is related to polarizability (α), which, in turn, is also proportional to molar refractivity (n). This results in the relationship between dielectric constant and molar refractivity of $n^2 \approx \varepsilon$[12]. Molar refractivity of chlorine is about 9.0 while those of fluorine, carbon, and hydrogen are 0.81, 2.59 and 1.03, respectively[6]. As a result, chlorine incorporation increases the dielectric constant, while fluorine decreases it. We observed cyclic imide C-N stretching at 1340~1360cm^{-1} and carbonyl C=O stretching at 1700cm^{-1}, [10,13] both of which increased in intensity with Cl_2/N_2 and Cl_2/O_2 plasma treatment, respectively. The high polarity of the newly incorporated N_2 or O_2 is speculated to increase the dielectric constant of the polyimide film. When the surface of as-cured polyimide is exposed to Cl_2/O_2 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_2/O_2 plasma, which could cause the degradation of the dielectric properties of polyimide[14].

XPS analysis was conducted to investigate the chemical configuration of the film more closely. The XPS spectra in Figs. 5(a) and 5(b) show a considerable incorporation of Cl and F into polyimide films after Cl_2 and SF_6 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_2-plasma-treated polyimide in Fig. 6(a) shows a peak at 286.6eV which is possibly due to C-C, C-H or C-N bonds. The second feature at 287.1eV indicates the existence of chlorobenzene, and the highest binding energy feature at 289.7eV is assumed to be from carbonyl carbon[13,15]. Figure 6(b) for SF_6-plasma-treated polyimide shows a peak at 287.8eV which is attributed to the emission from C-C, C-N, or C-O bonds. The feature at 289eV is probably due to $\underline{C}F$-CF_2, CF_3-$\underline{C}$-CF_3, -CF-$\underline{C}F$-CF-, and the highest binding energy at 291.4eV is likely due to $\underline{C}F_2$-CF, $\underline{C}F_2$-CF_2, CF-$\underline{C}F_2$-CF or -CF_2-$\underline{C}F_2$-CF_2- [13,15].

Even though SF_6 plasma cannot be used for Al etching due to the formation of nonvolatile etch products[16], it is effective in terms of decreasing the dielectric constant of polyimide. In addition, SF_6 plasma shows a significantly higher polyimide etch rate than Cl_2 plasma (Fig. 7). The optimal combination of these two

plasma processes will be a good tool in realizing multilevel metallization structures utilizing polyimide as the ILD layer.

4. Conclusions

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

(1) The Cl-based plasma used for Al etching causes the problem of increasing the dielectric constant of polyimide.

(2) The dielectric constant of polyimide is effectively reduced by exposure to SF_6 plasma.

(3) The leakage current density of polyimide is decreased after plasma exposure.

(4) Chlorine and fluorine atoms form chemical bonds with polyimide, as shown by FTIR and XPS.

(5) The etch rate of polyimide is much higher with SF_6 plasma than with Cl_2 plasma.

(6) Multilevel metallization could be performed by an optimized plasma process with Cl_2 in combination with SF_6.

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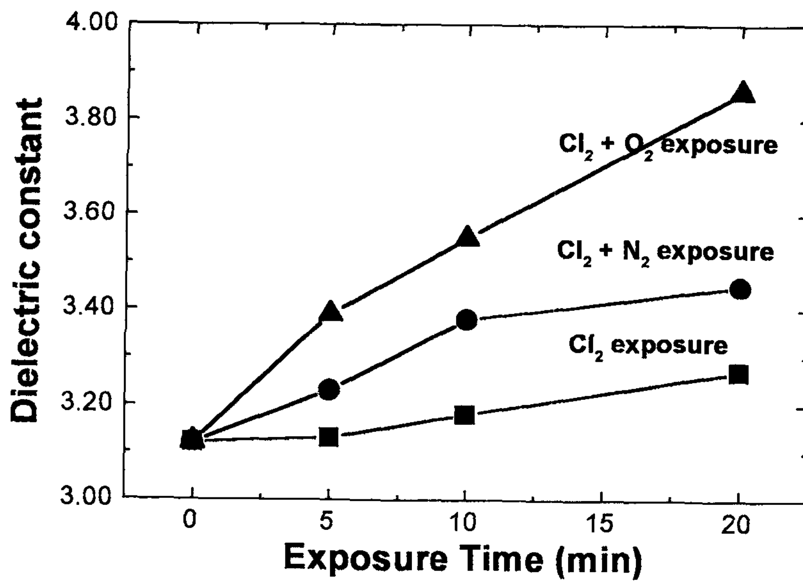


Figure. 1 Variation of polyimide' s dielectric constant during exposure to Cl-based plasma.

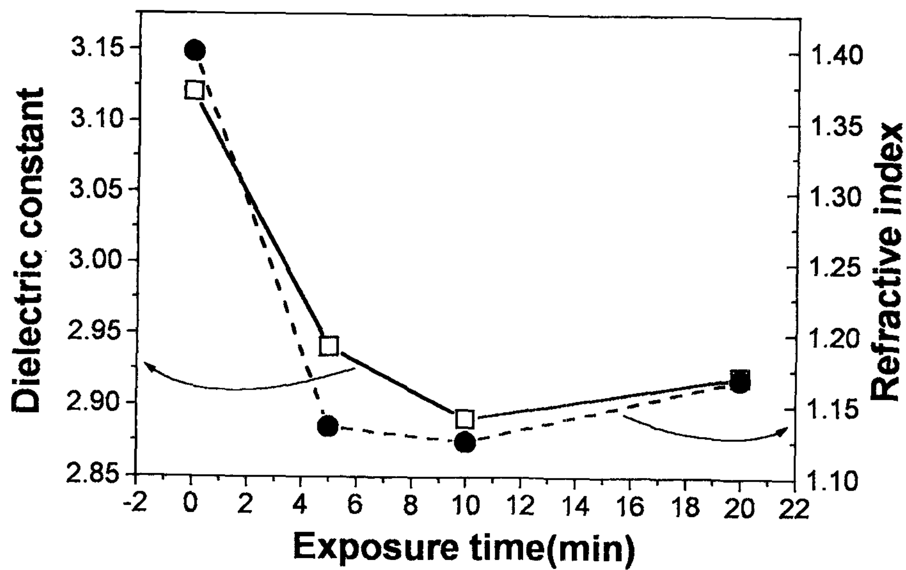


Figure. 2 Dielectric constant and refractive index of polyimide as a function of exposure time to SF_6 plasma

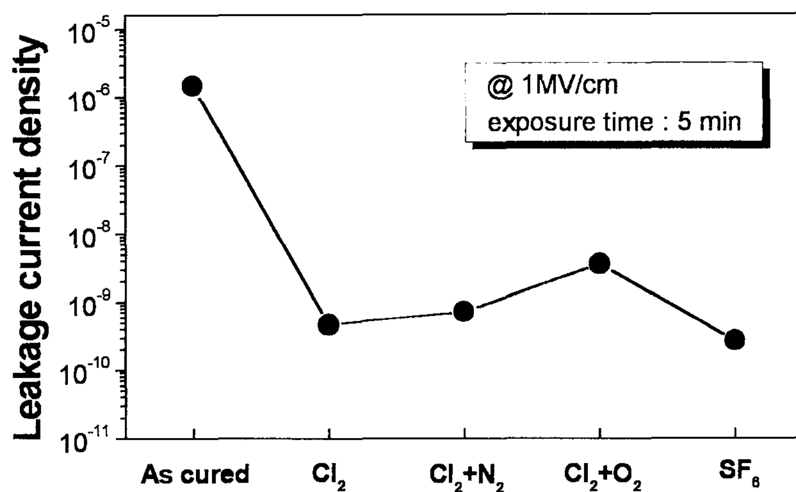


Figure. 3 Leakage current density of polyimides after exposure to various plasma.

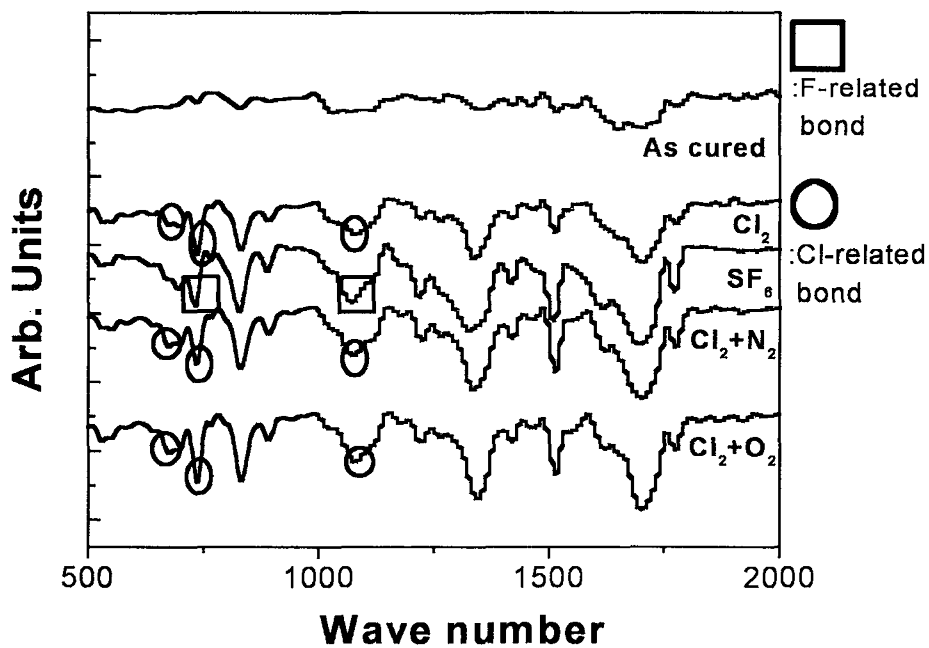
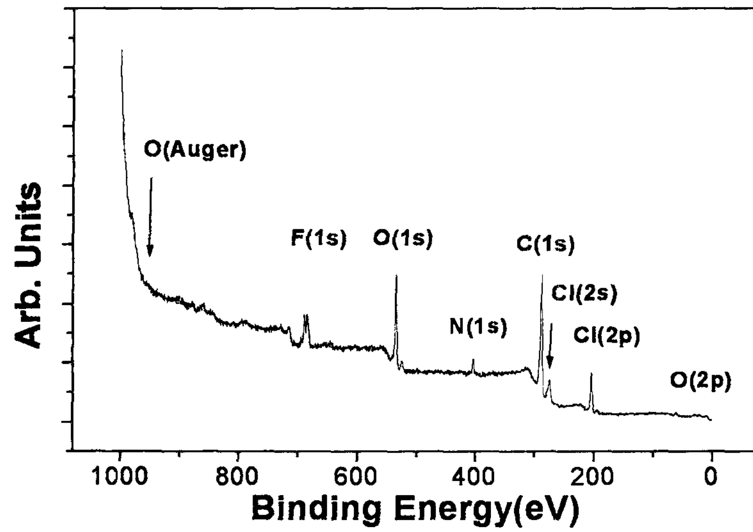
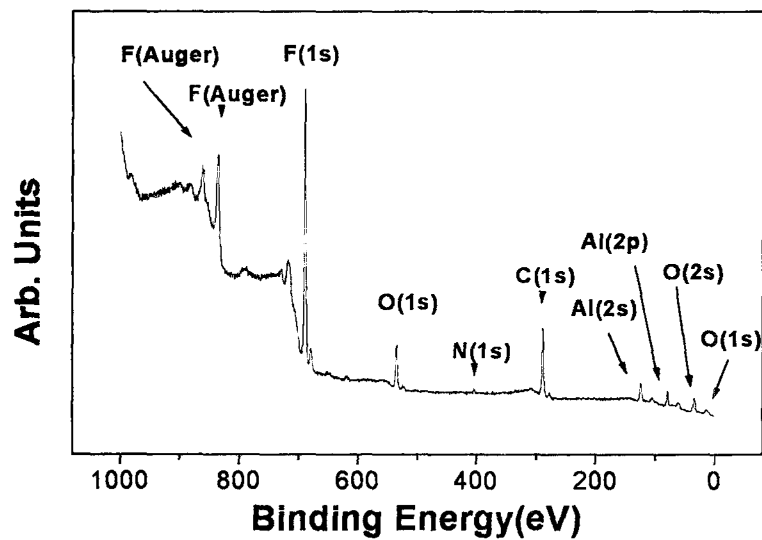


Figure. 4 Infrared spectra of polyimides exposed to various plasmas.



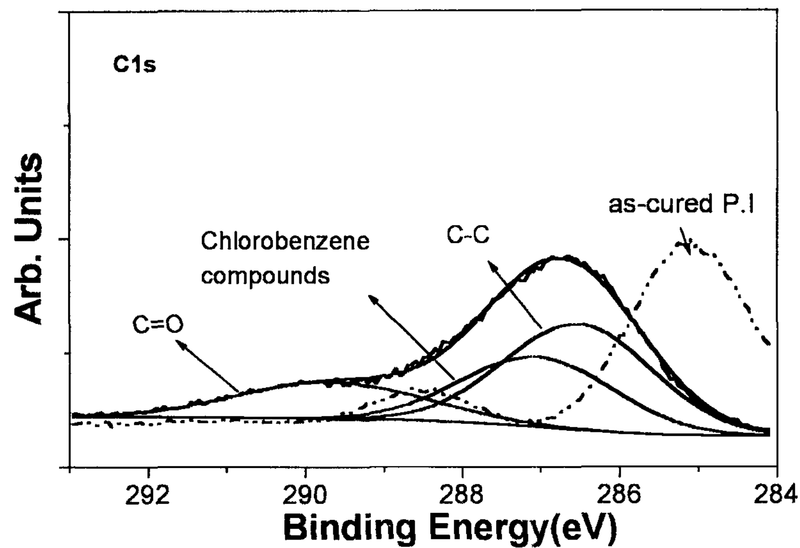
(a)



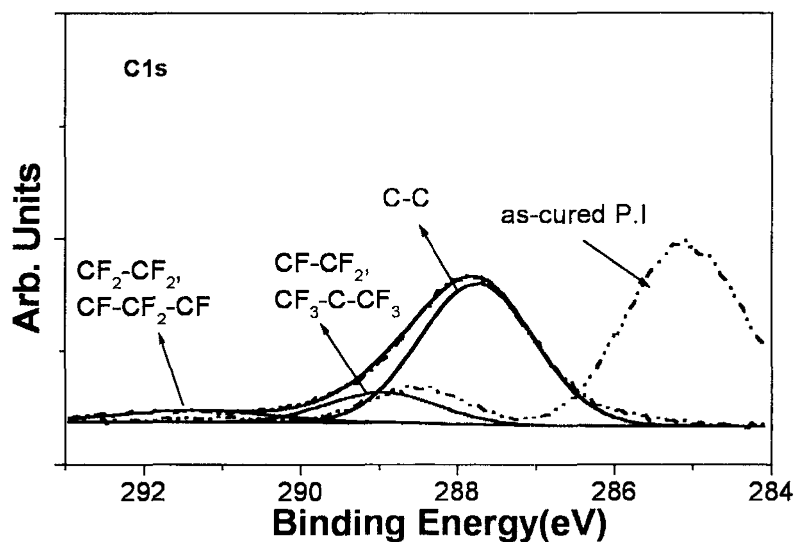
(b)

Figure. 5 XPS spectrum of polyimide exposed to Cl_2, SF_6 plasma.

Wide scanning showing (a) chlorine incorporation (b) fluorine incorporation



(a)



(b)

Figure. 6 XPS spectrum of C 1s and deconvoluted spectra. (a) as cured polyimide and polyimide exposed to Cl_2 plasma, (b) as cured polyimide and polyimide exposed to SF_6 plasma.

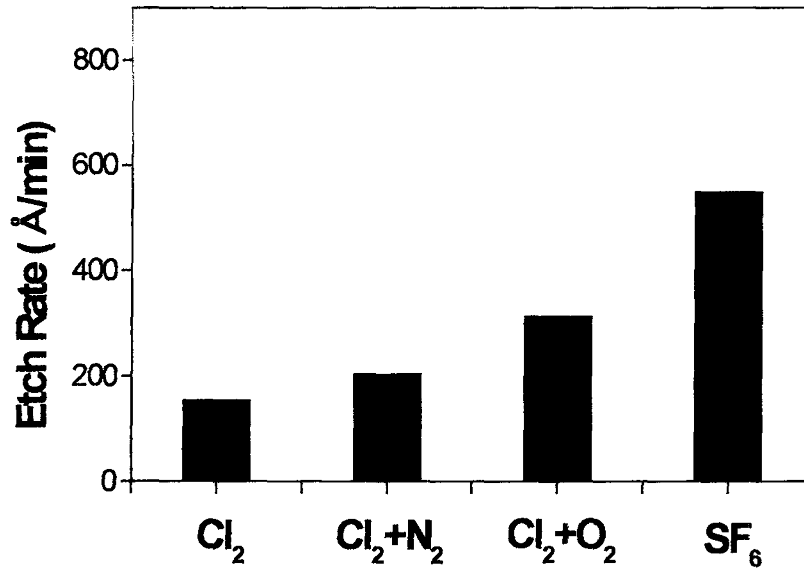


Figure. 7 Etch rate of polyimide by various gas composition with ECR plasma etching system