Low Df Polyimide with Photosensitivity for High Frequency Applications

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We have investigated molecular motion and polarity of polyimide chain to developed novel low dielectric constant (Dk) and dissipation factor (Df) polyimides. We found that Df at 10-100 GHz corresponds molecular mobility at -150 to -50 ℃. To reduce the dielectric loss (=Df) at high frequency, restriction of molecular motion at low temperature was important. In addition, to reduce polar and flexible unit in the polyimide chain is also important to obtain low Dk and Df polyimide. We exploited these knowledge for development of low dielectric loss polyimide for RDL. As the result, we achieved 0.002 of loss tangent and 2.7 of dielectric constant respectively about novel polyimide. Those polyimides are patternable by alkaline wet etching with positive photo-resist development and by UV laser ablation method. We also have developed photo-definable low loss tangent polyimide by blending of photo active reagent. Lower insertion loss of microstrip line was observed by the novel low Df polyimide than by conventional photosensitive polyimide. Those low dielectric loss polyimides are suitable for insulator of FO-WLP, interposer and other RF applications for microelectronics.

Keywords: Polyimide, Low Dk & Df, High frequency, Patterning, Low insertion loss

1. Introduction
Recently, technology for 5G communication using the higher frequency is pushed forward for realization of the high-speed large-capacity communication [1]. In addition, frequency over 60 GHz will be used in the millimeter wave radar which is utilized for the collision-avoidance system of the car [2]. A fan-out wafer level package (FO-WLP) attracts attention about the package of the semiconductor for package size and the fabrication cost reduction. The insulator materials having low dielectric constant (Dk) and dissipation factor (Df) are necessary for redistribution layers (RDLs) in the FO-WLP with high frequency [3]. In particular, antenna in package (AiP) with fan-out technology is one of key technology for 5G era. Polytetrafluoroethylene and a liquid crystal polymer are known as a low dielectric constant, low dielectric loss materials. However, these have difficulty in those poor adhesion and patternability with fine pattern. Photo BCB which was applied for re-distribution layer of FO-WLP is low dielectric constant material [4]. However, the BCB has poor mechanical properties and narrow process window.

Basically polyimide shows good thermal stability, excellent mechanical properties and relatively good adhesion to various materials. These background motivated us to develop low Df polyimide. In this paper, we developed novel low Dk and Df polyimide with patternability by various equipment. We found that low polarity and molecular mobility is important for low Dk and Df polyimide. The novel polyimide is patternable with UV laser tool. We also developed negative tone photosensitive low Dk and Df polyimide.

2. Experimental
2.1. Polyimide preparation
Polyimide resin was obtained by polycondensation of tetracarboxylic dianhydrides and diamines with solvent under nitrogen atmosphere. The fixed amount of diamines were placed in a 4 neck flask with a mechanical stirrer, thermometer and nitrogen inlet. Then N-methyl-2-
pyrridone (NMP, Mitsubishi Chem.) was added to the flask. Then, the flask was heated to 60 °C under nitrogen flow. The fixed amount of tetracarboxylic dianhydrides were added to the diamines solution with NMP. The mixture was stirred for 1 hour at 60 °C, then heated to 180 °C. Polycondensation reaction was carried out at 180 °C for 4 hrs.

2.2. Photosensitive polyimide solution preparation
Photosensitive polyimide solution was obtained by following procedure. 10 g of polyimide was measured then dissolved in a gamma-butyrolactone (GBL, Mitsubishi Chem.) at 35 wt% concentration. 1-5 wt% of photo initiator and 10-40 wt% of cross-linker were added to the solution. The obtained solution was filtered by PTFE filter prior to use.

2.3. Measurement of dielectric properties
Polyimide solutions were coated on a 6-inch Si wafer by a spin coater at 10 μm after cure. The coated wafer was soft-baked at a hot-plate 120 °C for 3 min. When the coated material was photosensitive, 1500 mJ/cm² UV (i-line energy) was exposed. Then the wafer was heated at 220 °C for 1 hr under N₂ flow. Polyimides films were obtained from cured wafer with immersing HF solution at room temperature for 10 min.

The obtained film was dried by 200 °C for 1hr in a convexion oven. Dielectric properties were measured by using the cured film by TMR-1A (Keycom, Cavity resonation method) at 1 GHz or 20 GHz.

2.4. Dynamic mechanical analysis (DMA) measurement
50-μm thick polyimide film was obtained as previous section. The polyimide film was set in a DMA equipment (Rheogel-E4000, UBM) and measured storage modulus and loss modulus of 1-64 Hz from -150 °C to 100 °C with 1.5 °C/min heating rate under N₂ flow.

2.5. Patterning process
Detail conditions and equipment are shown in Figs. 6~8 on section 3.

2.6. S-parameter measurement
Polyimide film was fabricated on glass/Cu substrate by similar procedure on section 2.3. Via hole was formed by UV laser equipment. Then, seed layer (Ti and Cu) was sputtered. Patterned photoresist was fabricated by photolithography method. Then, electroplating with cupric sulfate and sulfonic acid aqueous was conducted. After photoresist was removed by remover, seed layer was etched by etchant. S-parameter was measured by vector network analyzer.

3. Results and discussion
Basically, polyimide shows larger Dk and Df due to carbonyl moiety derived from carboxylic acid. On the other hand, polyimide shows good thermal stability, mechanical properties, adhesive properties. That is reason why polyimide is applied for microelectronics applications. This is a motivation that we started to investigate polyimide structure to decrease dielectric properties. In this section, we discuss molecular structure of polyimide for low dielectric properties and demonstrate patterning method of the polymer.

3.1. Polarity and molecular mobility study
We focused on polarity of polyimide in order to decrease Dk and Df value of polyimide. An aromatic common polyimide is composed of aromatic dianhydride (ex. pyromellitic dianhydride (PMDA)) and aromatic diamine (ex. 4,4'-oxydianiline (ODA)) (Fig. 1). We prepared a low polar polyimide where some (30 mol%) of siloxane moiety was introduced and the common polyimide (Fig. 2). Interestingly, low polar polyimide with siloxane back-bone showed lower Dk and larger Df comparing that of the aromatic common polyimide (Table 1).

![Fig. 1. PMDA-ODA polyimide.](image1)

![Fig. 2. Low polar polyimide with siloxane back-bone.](image2)

| Table 1. Dielectric properties of polyimides. |
|-----------------------------------------------|
| Polyimide       | poly(PMDA-ODA) | Siloxane Polyimide | Rigid Polyimide |
|-----------------|----------------|--------------------|-----------------|
| Dk (1 GHz)      | 3.2            | 2.9                | 3.3             |
| Df (1 GHz)      | 0.008          | 0.01               | 0.004           |
We measured DMA from low temperature (-150 °C) to 200 °C to analyze relaxation by molecular motion in order to understand why less polar siloxane group affect to increase the Df. We made master curve of polyimides regarding to time-temperature superposition principle. According to the principle, master curve offers viscoelastic information of the polymers under high frequency stimulation which we cannot measure at due to equipment limitation. DMA results and modulus-frequency dispersion data are shown in Figs. 3 and 4.

In case of poly(PMDA-ODA), no relaxation was observed from -150 °C to 100 °C. Frequency dispersion curve was also nearly flat (Fig. 3). On the other hand, we observed large relaxation around -100 °C in case of siloxane polyimide. We found tan δ (=E’/E’’) peak around 100 GHz order from master curve. The tan δ peak corresponds to about -100 °C dispersion in DMA. We expect that dispersion of origin in DMA is molecular motion of soft siloxane unit due to its glass transition. So, restriction of molecular motion is quite important to obtain low tan δ polyimide at high frequency.

Next step, we examined effect of polyimide molecular mobility. Figure 5 shows frequency dispersion curve derived from DMA result of polyimides that siloxane (red) and rigid (green) unit are introduced into. We found the rigid polyimide showed no relaxation and lower tan δ than siloxane polyimide. This result indicates flexibility of siloxane unit affected to larger Df value. In addition, the rigid polyimide showed smaller dielectric loss comparing the reference common polyimide (Table 1). This result indicates tan δ at high frequency estimated by master curve of DMA result has good correlation to dielectric loss at the same high frequency. According to result shown in Table 1 and Fig. 5, introduction of rigid and less polar unit in polyimide structure is prospective method to obtain low Dk and Df polyimide.
3.2. Development of novel low Dk and Df polyimide

From those observations in previous section, we made two molecular design strategies. One is control of molecular motion in polyimide backbone and another is less polarity. After all, we developed three types of the low Dk and Df polyimide.

Properties of developed polyimide is summarized in Table 2. PI-A can be patternable by alkaline wet etching with photo resist. Because PI-A has acid functional group in side chain, it is soluble in alkaline developer. Cured film of PI-A, PI-B and PI-C can be patternable by UV laser drilling method. PI-C contains photo initiator and cross linker to obtain photolithographic property. All of the three polyimide can be cured under lower temperature below 250 ℃. Low temperature curable property is one of the important for redistribution application of semiconductor package. Moisture uptake is relatively lower than common polyimide. Elongation of PI-A and PI-C are enough high for insulator multilayer Cu interconnection. We confirmed chemical resistance of PI-B and PI-C. Both showed good resistivity to NMP and stripper which is DMSO-TMAH solution.

3.3. Patterning result of novel low Dk and Df polyimide

We demonstrated three types patterning process using novel polyimide material. PI-A can be patterned by alkaline wet etching with novolac photoresist. PI-A dissolves in alkaline aqueous and is not soluble in some organic solvent (ex. butyl acetate) which photoresist dissolves in. Because of this feature of solubility of PI-A, PI-A is patternable by wet etching process. Result of patterning by wet etching is shown in Fig. 6. When photoresist is developed, PI-A is etched simultaneously. After photoresist removal, patterned PI-A can be cured.

All of the three novel polyimides can be patternable by UV laser (wavelength 248 nm, KrF excimer laser) drilling method. Process flow and result of laser patterning by excimer laser are shown in Fig. 7. A 5-μm via hole was opened. Because most of polyimides can be selected, UV laser drilling method is one of the best process to make fine patterning be compatible with low Df. We also confirmed it was possible for the novel polyimide to be patterned by YAG laser whose wavelength is 355 nm.

PI-C which contains photo initiator and cross linker is negative tone photo definable materials. PI-C has slight larger Df value due to components for photolithography. Regarding to semiconductor and other electronic components, not only liquid coating materials but also B-stage sheet materials for dielectric materials are important. In case of PI-C, we demonstrated negative-tone photo sensitive material of B-stage sheet (Fig. 8). PI-C offered fine

| Table 2. Properties of low Dk & Df Polyimides. |
|-----------------------------------------------|
| Patterning method | PI-A | PI-B | PI-C |
| Dk (20 GHz) | Wet Etch / Laser | Laser | Photo-Litho. / Laser |
| Df (20 GHz) | 3.0 | 2.7 | 2.7 |
| Tg (℃) | 145 ℃ | 175 ℃ | 120 ℃ |
| CTE | 70 ppm | 65 ppm | 70 ppm |
| Young’s Modulus | 2 GPa | 1.9 GPa | 1.7 GPa |
| Tensile Strength | 100 MPa | 95 MPa | 65 MPa |
| Elongation | 150 % | 40% | 15% |
| Moisture uptake | 0.6% | 0.6% | 0.6% |
| Cure Temp. | 220 ℃ | 220 ℃ | 200 ℃ |
| Chemical Resistance | NMP b) | - | <+5% |
| (Thickness change) | Stripe b) | - | <+5% |

a) Result of 1 GHz. b) Test condition: 40 ℃/10 min.
pattern of 10-μm space and 20-μm via hole by broadband exposure and organic solvent development. The advantage of PI-C is conventional photo lithographic tools are compatible to this material.

3.4. S-parameter measurement with microstrip line
Microstrip line was fabricated to measure S11 and S21 parameter using novel low Df polyimide (PI-A) and our conventional photo definable polyimide (Photo-PI) [5]. Thickness of insulator (PI-A & Photo-PI) was around 25 μm. Length, height and width of the Cu wire were 10 mm, 10 μm and 60 μm, respectively. Via hole size was 30 μm (Fig. 9). Figure 10 shows the frequency dependence of insertion and return losses.

Fig. 6. (a) Patterning process flow, (b) patterning conditions and result of wet etching (PI-A).

Fig. 7. (a) Patterning process flow, (b) patterning conditions and result of laser drill (PI-B).

Fig. 8. (a) Patterning process flow, (b) patterning conditions and result of photo-lithography (PI-C).

Fig. 9. (a) Schematic illustration of microstrip line (cross section view), (b) picture image of microstrip line (over view).

Fig. 10. (a) S21-parameter vs frequency of microstrip line using PI-A(red) and photo-PI(orange). (b) S11-parameter vs frequency of microstrip line using PI-A(green) and photo-PI(blue).
The insertion losses regarding to S21 parameter spectra show serpentine shape due to impedance mismatching. Maximum value of S21 parameter is corresponding to bottom of S11 parameter at resonated frequency. Insertion loss of PI-A at 20 GHz and 30 GHz were around 0.8 dB and 1.0 dB, respectively. Those value are one half lower than result of Photo-PI. We demonstrated PI-A offered lower insertion loss than conventional polyimide at high frequency signal.

Since our novel low Df polyimides show excellent properties (low dielectric loss, high elongation, good patternability, etc.), those low dielectric loss polyimides are useful for insulator of FO-WLP, interposer and other RF applications of microelectronics.

4. Conclusion

We have developed novel low Dk and Df polyimides by investigation of molecular motion and polarity of polyimide chain. According to DMA measurement, it is important to suppress molecular motion at low temperature around -100 ℃ for Df reduction at high frequency. In addition, to decrease polar and flexible unit in the polyimide is also important to obtain low Dk and Df polyimide. As the result, we achieved 0.002 of loss tangent and 2.7 of dielectric constant respectively. We demonstrated three type of patterning process for the low Dk and Df polyimide. PI-A is patternable by alkaline wet etching with positive photo-resist development. PI-C which is negative tone photo-definable is compatible to conventional photo lithography tool. All of novel low Df polyimide can be patterned by UV laser drilling method. The novel polyimide showed lower insertion loss of microstrip line than conventional photo-PI. Those low dielectric loss polyimides are useful for insulator of FO-WLP, interposer and other RF applications for microelectronics.

References and note
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5. Dielectric properties of “Photo-PI” are Dk=3.2 and Df=0.03 @1GHz.