Development of Low Dk and Df polyimides for 5G application

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Abstract

We have newly developed non photosensitive and photosensitive polyimide having excellent electrical/mechanical properties. At first we have re-designed the polymer backbone in order to obtain low Dk and Df performance. As a result, our new non photosensitive PI achieved 2.9 of Dk at 20 GHz and 0.003 of Df at 20 GHz. In the next step, we selected the photo package of new PI carefully to maintain both low Dk/Df and high resolution. After that, we modified the photo initiator content, crosslinker content, and so on to have both high lithographic performance and high electrical performance. As a result, new photosentive PI cured at 320 °C showed 3.0 of Dk at 20 GHz and 0.006 of Df at 20 GHz. In addition, this material cured at 200 °C also showed 3.0 of Dk at 20 GHz and 0.009 of Df at 20 GHz. We also confirmed high mechanical properties of new PI. Elongation of this PI cured at >250 °C was approximately 70 %. From lithographic aspects, new PI achieved 15 μ m L/S opening with 10 μ m thickness.

Key words

Low Dk, Low Df, Photosensitive, Polyimide

I. Introduction

The next generation of broadband telecommunication 5G is being paid much attention in order to meet the requirements for boosting signal transmission rate and managing a huge data flood. Various development works relating to 5G including data processing, electronics package, materials, and so on have been reported recently [1].

With regards to electrical performance of insulation materials, low Dk (dielectric constant) and Df (dielectric loss) performances are highly preferred for 5G application. From this view point, polytetrafluoroethylene (PTFE) or benzocyclobutene (BCB) look promising and being tried to use in electronics packages. However, these materials don't have enough adhesion or mechanical properties to ensure the reliability of the packages [2], [3].

On the other hand, polyimides (PIs) have been widely used for electronics packages owing to excellent adhesion and mechanical/thermal performances [4]-[11]. Especially, photosensitive PIs also have an advantage of easier assembly processing and that's why photosensitive PIs are now being adopted for dielectrics use of re-distribution layers in wafer level packages (WLPs). However, in terms of expanding the versatility of photosensitive PIs to 5G application, further improvement of Dk and Df is strongly required with keeping the other performances good.

In this paper, novel non photosensitive and photosensitive

polyimide with excellent electrical/mechanical properties will be introduced for 5G applications. It should be noted that the novel non photosensitive PI achieved 2.9 of Dk at 20 GHz and 0.003 of Df at 20 GHz. The novel negative-tone solvent developable PI cured at 375 °C achieved 3.0 of Dk at 20 GHz and 0.005 of Df at 20 GHz. In addition, this material cured at 200 °C showed 3.0 of Dk at 20 GHz and 0.009 of Df at 20 GHz as well.

II. Experimental

A. Polymer synthesis

The polyamic acid was prepared in N-methylpyrrolidone through isoimide method by using tetracarboxylic acid dianhydride and diamine as a starting material. The reacting solution obtained was poured into water and the resulting polymer was filtrated and dried under vacuum.

B. Preparation of photosensitive PI varnish

Photosensitive negative-tone PI varnishes were prepared by mixing PI precursor, cross-linker, photo initiator and other additives in solvent.

C. Evaluation of lithographic performance

Photosensitive negative-tone PI varnishes were coated on 6-inch silicon wafers and baked at 80 °C/ 100 s + 90 °C/ 100

s (Tokyo Electron Act 8). The coated films (10 to 12 μ m thickness) were exposed through a mask using an i-line stepper (Canon FPA-3000iW) and developed with cyclopentanone. Then the wafer was cured at a given temperature (Koyo μ -TF). The resolution of the resulting patterns was measured by using an optical microscope.

D. Evaluation of cured film performance

Cured film properties of PI such as Tg, modulus, and elongation were measured by using cured film which was obtained by peeling off from Si wafer by treatment with diluted HF.

E. Evaluation of Dk/Df performance

The cured PI film was prepared on Si wafer regardless of photosensitivity. After peeling off the PI film from Si wafer, The Dk and Df value of the PIs were evaluated by Split Post Dielectric Resonator (SPDR) method.

III. Results and discussion

Design concept of Low Dk/Df PI

We synthesized various non-photosensitive and photosensitive polyimide backbones and evaluated the Dk/Df performance. The polarity and molecular motion of dianhydride (A1 to A3) and diamine (B1 to B3) are summarized in Table 1 and results are also summarized in Table 2.

Acid/amine	Name	Polarity	Molecular motion
Dianhydride	A1	Low	High
Dianhydride	A2	Middle	Low
Dianhydride	A3	High	Middle
Diamine	B1	Low	Middle
Diamine	B2	High	Low
Diamine	B3	Middle	High

Table 1. Features of diacid/diamine used in this study

Table 2. The effect of polyimide structure on Dk/Df.

Run	Acid	Amine	Dk at 20 GHz	Df at 20 GHz
1	A1	B1	3.0	0.004
2	A2	B1	3.1	0.010
3	A3	B1	3.2	0.004
4	A1	B2	3.3	0.008
5	A1	B3	3.0	0.009

As a result of Run 1 to Run 3, the Dk value of resultant polyimide was affected by polarity of monomers. Run 1 showed the lowest Dk. In addition, the Df value was changed by amine structure. By selecting B1 as diamine, we could achieve low Dk and Df probably due to combination of low polarity and middle molecular motion. As a conclusion, we found that selection of monomers with low polarity and low molecular motion was important for achieving low Dk/Df PI.

Non photosensitive PI with low Dk/Df performance

In order to achieve non photosensitive low Dk/Df PI, we synthesized two kinds of polyimide with similar design concept based on the discussion above. The effect of curing temperature on Dk and Df at 20 GHz are summarized in Figure 1 and Figure 2.

As a result, Dk was not affected by curing temperature. So Dk of polyimide depends on polyimide structure itself. On the other hand, Df was changed and decreased as increasing curing temperature probably due to high interaction between polymers obtained. NPD (Non Photo Definable) PI 1 cured at 200 $^{\circ}$ C achieved 2.9 of Dk and 0.005 of Df. NPD PI 2 cured at 250 $^{\circ}$ C also achieved 2.9 of Dk and 0.003 of Df, respectively.



Figure 1. Impact of curing temp. on Dk for NPD PI.



Figure 2. Impact of curing temp. on Df for NPD PI.

Photosensitive PI with low Dk/Df performance

Addition of photosensitivity to the polyimide for low Dk/Df application was studied in this report. Firstly, the polymer backbone for low Dk/Df NPD PI was modified by adding crosslinking moiety to the polymer. Then the polymers, crosslinker, photo initiator, and so on were mixed in a solvent. After filtration, these varnishes were evaluated

from the view point of lithographic performance and cured film properties in addition to electrical performance.

The effect of curing temperature and cross linker content on Dk and Df at 20 GHz are summarized in Figure 3 and Figure 4.



Figure 3. Impact of curing temp. and crosslinker content on Dk for PDPI.



Figure 4. Impact of curing temp. and crosslinker content on Df for PDPI.

As a result, Dk was not changed by increasing curing temperature or increasing crosslinker amount from 0.5X to 2X. On the other hand, Df value was decreased as increasing curing temperature. In addition, Df value was increased as increasing crosslinker content. Basically we expected that low loading of crosslinker was needed to maintain the low Dk/Df performance, however there was no relationship between crosslinker content and curing temperature on Dk performance. Contrastively we found that it was necessary to keep low amount of additives for lower Df value.

We also evaluated the lithographic performance of Photo Definable(PD)PI for low Dk/Df application. The effect of irradiation dose on film retention is summarized in Figure 5. The new PI achieved >80 % film retention after development which is enough for practical use.



Figure 5. Film retention of PDPI.

We also confirmed the resolution of L/S pattern and via for this polyimide. Results are shown in Figure 6. The lithographic performance of new PI was as same as that of conventional PI even though Dk/Df performance of new PI was better than conventional PI. 15 μ m L/S and 30 μ m via were achieved by using new PI.



Figure 6. Patterns on Si wafer. Film thickness: 10 µm.

The mechanical property of new PI was also evaluated. Results are shown in Figure 7. We found high mechanical properties of cured new PI. Especially, elongation of new PI cured at >250 °C was around 70 %.



Figure 7. Mechanical properties of cured new PI

III. Conclusion

We have developed non photosensitive and photosensitive PI with low Dk and Df performance. At first we have re-designed the polymer backbone of non photosensitive PI from the view point of polarity and molecular motion. As a result, our new non photosensitive PI achieved 2.9 of Dk at 20 GHz and 0.003 of Df at 20 GHz. Then, we modified this polymer backbone to add crosslinking moiety. As a result, new photosensitive PI cured at 320 °C showed 3.0 of Dk at 20 GHz and 0.006 of Df at 20 GHz. In addition, this material cured at 200 °C also showed 3.0 of Dk at 20 GHz and 0.009 of Df at 20 GHz. We also confirmed high mechanical properties of new PI. Elongation of this PI cured at >250 °C was approximately 70 %. As a lithographic performance, new PI achieved 30 μ m via opening with 10 μ m thickness.

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