Photosensitive Polyimide having low loss tangent for RF application

Masao Tomikawa, Hitoshi Araki, Yohei Kiuchi, and Akira Shimada
Electronic & Imaging Materials Research Laboratories,
Toray Industries
3-1-2 Sonoyama, Otsu-City, Shiga-Ken 520-0842, Japan
Phone: +81-77-533-8716
Masao_Tomikawa@nts.toray.co.jp

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

Abstract

Progress of 5G telecommunication and mm radar for autopilot, high frequency operation is required. Insulator materials having low loss at high frequency is desired for the applications. We designed the low dielectric constant, and low dielectric loss materials examined molecular structure of the polyimide and found that permittivity 2.6 at 20GHz, dielectric loss 0.002. Furthermore, in consideration of mechanical properties such as the toughness and adhesion to copper from a point of practical use. Dielectric properties largely turned worse when giving photosensitivity. To overcome the poor dielectric properties, we designed the photosensitive system. After all, we successfully obtained 3.5 of dielectric constant and 0.004 of dielectric loss, and 100% of elongation at break. In addition, we offered a B stage sheet as well as varnish. These materials are applicable to re-distribution layer of FO-WLP, Interposer and other RF applications for microelectronics.

Introduction

Toward an establishment of the high-speed large-capacity communication, practical use of the communication in the 5G technical format to use the higher frequency for is pushed forward [1]. In addition, frequency more than 60GHz is used in the millimeter wave radar which is effective for the collision avoidance of the car [2]. In order to decrease its size, a fan-out type wafer level package (FO-WLP) attracts attention about the package of the semiconductor. The insulator materials having low permittivity, dielectric loss are necessary for rewiring of this inside to use the FO-WLP with high frequency [3].

Polytetrafluoroethylene and a liquid crystal polymer are known as a low dielectric constant, low dielectric loss materials, but these have difficulty in those poor adhesiveness, poor fine pattern formation. Photo BCB was applied for re-distribution layer of FO-WLP [4]. However, the BCB has poor mechanical properties and narrow

process window.

We designed the low dielectric constant （Dk）, and low dielectric loss（Df） examined molecular structure of the polyimide and found that 2.9 of Dk at 20GHz, and 0.003 of Df by polyimide structure design. Furthermore, in consideration of mechanical characteristics such as the large elongation at break, adhesion to copper, polymer structure and photosensitive system dependency were investigated. An electric nature basically turned worse when adding a photosensitivity.

2.Experimental

2.1Polyimide synthesis

Polyimide prepolymer (poly(amic acid) (PAA)) was obtained by reaction with dianhydrides and diamines in a N-methyl-2-pyrollidone (NMP, Mitsubishi Chemical) under N_2 flow.

2.2Photosensitive polyimide preparation

A. Positive tone type

Partial esterified PAA was obtained by reaction with PAA and dimethylformamide dimethylacetal (DFA) at 50C for 2hrs. The esterified PAA was precipitated in water. The precipitated polymer was dried at 80C for 48hrs. The dried esterified PAA (10g), diazonaphthoquinone compound (PA-280, Merck, 2g) and KBM-403 (Shinetsu silicone, 0.1g) were dissolved into gamma butylolactone (GBL) at 30wt%. The obtained solution was used as a positive photosensitive polyimide.

B. Negative tone ionic bonded type

Dimethylaminoethylmethacrylate (DMM, Wako Chemical, 5g), and 0.2g of dimethylamino benzophenone (TCI) were dissolved into 30g of PAA solution. The obtained solution was used a negative tone ionic bonded photosensitive polyimide.

C. Negative tone ester type

Dianhydride (0.1mole) and hydroxyethylmethacrylate (HEMA, Wako Chemical, 26.0g (0.2mole)), and pyridine (Wako Chemical, 19.8g (0.2mole)) was dissolved into 100mL of NMP and stirred for 6hrs under dry air flow. After the reaction, the dianhydride solution was cooled below 10C by an icy bath. Dicyclohexyl carbodimide (DCC, TCI, 41.2g (0.2mole)) was dissolved into 40ml of GBL. The DCC solution was dropwised to the dianhydride solution slowly. Then diamine (0.1mole) was added to the solution and reacted for 6hrs under

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

dry air below 10C. After the reaction, the solution was filtered to remove by-product. Then filtrate was poured into 3L of 10% methanol containing water to obtain polymer precipitate. The polymer precipitate was washed by 10% methanol containing water for 3 times. Then polymer was dried into 50C convection oven for 72hrs.

Negative ester type photosensitive solution was prepared by addition of 10g the poly(amic ester) and 0.3g of photo initiator (OXE-02, BASF) in 30g of NMP.

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

2.3 Measurement of dielectric properties

Polyimide, and photosensitive polyimides were coated on a 6in. Si wafer by a spin coater at 10um after cure. The coated wafer was soft-baked at a hot-plate 120C for 3min. Then the wafer was heated at 350C for 1hr under N_2 flow. Polyimides films were obtained from cured wafer with immersing HF solution at room temperature for 10min.

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

Dynamic Mechanical Analysis (DMA) measurement

Polyimide film (50um thick) was obtained as previous section. The polyimide film was placed in a DMA (Rheogel-E4000, UBM) and measured storage modulus and loss modulus of 1-64Hz from -150C to 100C with 1.5C/min heating rate under N_2 flow.

3. Result and Discussion

3.1 Effect of polymer structure

Polyimide has 4 carbonyl groups in one acid moiety, usually polyimide shows larger Dk and Df. But polyimide performs good thermal stability, mechanical properties, adhesive properties, and so on. Polyimide is suitable for microelectronics applications due to those properties.

So we investigated an effect of polyimide structure on its dielectric properties. In order to obtain low Dk, Df polyimide, we focused on polarity of polyimide. Popular polyimide is composed of aromatic dianhydride (PMDA) and aromatic diamine (ODA) (Fig. 1). First some (30mol%) of less polar siloxane group was introduced into polyimide back-bone to reduce polymer polarity (Fig 2). Interestingly, siloxane containing polyimide shows lower Dk and larger Df comparing that of aromatic polyimide. To understand the why less polar siloxane group affect to increase the Df, we measured DMA from low temperature (-150C) to 200C to understand relaxation by molecular motion. DMA result is shown in fig. 3, large relaxation was observed about -100C. Probably the relaxation is thought to attribute glass transition of siloxane unit. By using the DMA data, we made modulus-frequency dispersion data shown in fig.4 [5]. In case of the soft siloxane polyimide, Df

peak around 100GHz order range was appeared. The Df peak is correspond to about -100C dispersion in DMA. We expect that dispersion of origin is molecular motion of soft siloxane unit due to its glass transition. So restriction of molecular motion is quite important to obtain low Df polyimide at high frequency.

Next step, we examined effect of polyimide molecular motion. To restrict the molecular motion, we add the rigid unit into polyimide back-bone (Rigid-PI). The Rigid-PI shows smaller Df comparing the reference aromatic polyimide.

From those observations, we designed the control of molecular motion and less polarity in polyimide back-bone. After all, we developed the low Df polyimde having 0.003 Df.

Table 1 Effect of polyimide structure on dielectric properties

Polyimide	**PMDA-ODA**	**Soft PI**	**Rigid PI**
Dk (1GHz)	**3.2**	**2.9**	**3.2**
Df (1GHz)	**0.008**	**0.01**	**0.003**

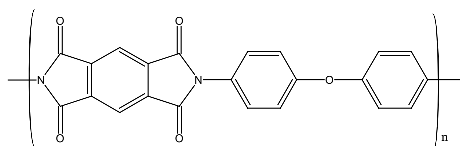


Fig.1 PMDA-ODA polyimide

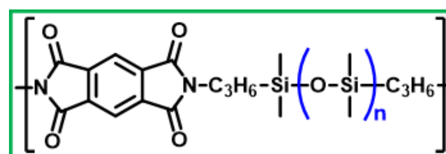
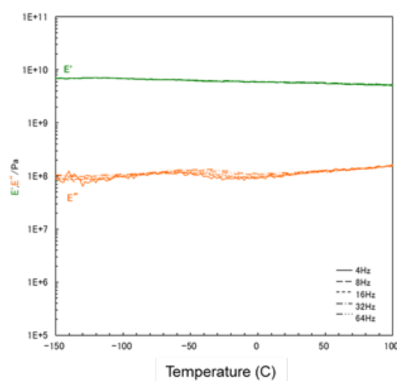


Fig. 2 Soft siloxane modified polyimide



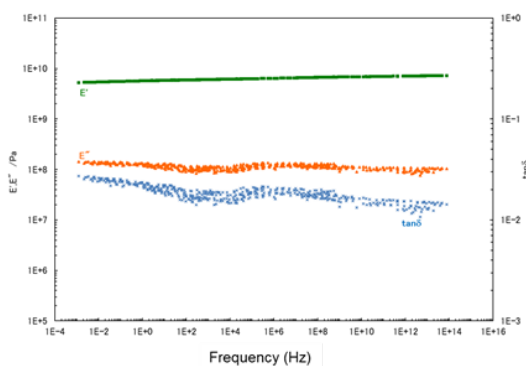


Fig. 3 DMA curve(Left) and Frequency dispersion curve(Right) of PMDA-ODA polyimide

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

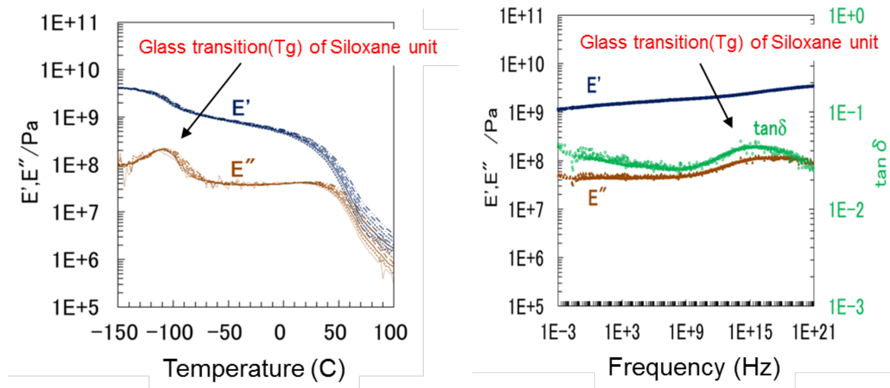


Fig.4 DMA curve(Left) and Frequency dispersion curve(Right) of soft siloxane modified polyimide

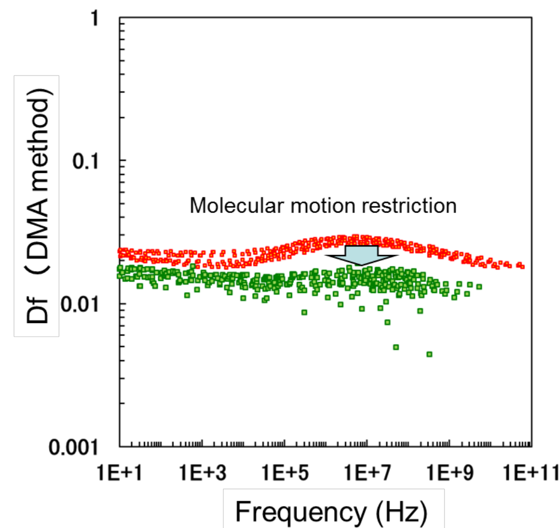


Fig.5 Effect of polyimide molecular motion on Df

Effect of Phosensitivity addition on Dk and Df

Addition of photosensitivity to polyimide is useful for practical use(). We investigated to add positive photosensitivity and negative photosensitivity. First we obtained the positive tone photosensitive polyimide by partial esterification method developed by authors [6]. So partial esterified poly(amic acid) was obtained by reaction with poly(amic acid) and DFA. Positive tone photosensitive polyimide was obtained by mixing with the partial esterified poly(amic acid) and diazonaphthoquinone photo active compound. The obtained positive photosensitive polyimide is difficult to obtain good pattern and larger Df (0.03).

Next we tried to obtain ionic bonded negative tone photosensitive polyimide. The ionic bonded negative photosensitive polyimide was obtained by mixing with poly(amic acid) and photo reactive

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

amine such as DMM and photo initiator such as bis(N,N-diethylaminophenyl)ketone [7]. The ionic bonded photosensitive polyimide shows relative low Dk and Df. But it is not easy to obtain good photo lithographic pattern by i-line. The Df of the ionic bonded photosensitive polyimide is 0.005.

Finally we prepared an ester linkage type negative photosensitive polyimide [8]. Preparation of the ester type negative photosensitive polyimide is relatively long and complicated. Initial Df of the ester type photosensitive polyimide was 0.02. We expected that HEMA ester and OXE-02 photo initiator was not decomposed completely. So HEMA contents in polymer and photo initiator were changed. To optimize the HEMA contents and photo initiator, we successfully developed the negative tone photosensitive low Df polyimide. The Dk and Df are 3.5 and 0.004 respectively. Comparing to genuine polyimide, Dk and Df are large. Finally photolithographic pattern of obtained low Df polyimides were shown in Fig. 6. Non photosensitive polyimide pattern was obtained by conventional wet etching process and laser drill process. Negative tone photosensitive polyimide pattern was obtained by similar process of photoresist. We will try to decrease Dk and Df as much as possible for next step.

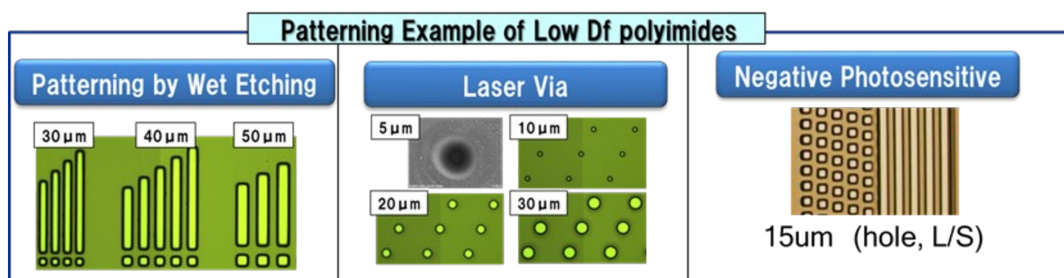


Fig. 6 Low Df polyimides pattern obtained by photolithographic process

Summary

In order to obtain low dielectric loss polyimide for RF applications, we investigated the effect of polyimide structure and photo sensitive systems. To control the molecular motion of polyimide, we obtained the novel polyimide having 2.9 of Dk and 0.003 of Df.

In addition, we developed negative tone photosensitive polyimide having 3.5 of Dk and 0.004 of Df. In addition, we have developed low cure temperature type polyimide having 3.0 of Dk and 0.003 of Df. Those Dk, Df and other physical properties were summarized in Table 2.

These developed materials are desired for insulators of promising RF telecommunication.

Table 2 Summary of this work

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022

		Non Photo PI	Non Photo PI (Low temp cure)	Photo PI
Base Resin		Polyimide	Polyimide	Polyimide
Dk	1GHz	2.8	3.0	3.5
	20GHz	2.9	-	3.5
Df	1GHz	0.003	0.003	0.004
	20GHz	0.003	-	0.004
Tg（℃）		224	145	237
CTE（ppm）		46	70	27
Strength（MPa）		136	98	176
Elongation（%）		110	201	58
Water Absorption（%）		0.6	–	0.6
Adhesion to Cu（N/mm）		6	-	6
Cure Temperature		350℃×1hr	220℃×1hr	350℃/1hr

References

[1] Y. Kishiyama, A. Benjebbour, S. Nagata, Y. Okumura, and T. Nakamura, “NTT DOCOMO 5G Activities –Toward 2020 Launch of 5G Services- “, NTT Docomo Tech. J., 23, 6 (2014)

[2]. T. Yamawaki and S. Yamano, “60-GHz Millimeter-Wave Automotive Radar”, Fujitsu Ten Tech. J. 11, 3 (1998)

[3]. D. Ishibashi, and Y. Nakata, “Terahertz Antenna Integration Module Using Fan-Out Wafer-Level Package Technology”, Fujitsu, 68, 65 (2017)

[4]. Y. Iseki, E. Takagi, N.Ono, J. Onomura, K. Yamaguchi, M. Amano, M. Sugiura, H. Yamada, Y. Shizuki, T. Togasaki, K. Higuchi, and K. Tateyama, “GaAs MMICs Using BCB Thin Film Layers for Automotive Radar and Wireless Communication Application”, Int. J. Microcircuits and Electronic Packaging, 23, 203 (2000)

[5]. J.D. Ferry, “Viscoelastic Properties of Polymers”, 3rd ed. Wiley & Sons (1980)

[6]. M. Tomikawa, S. Yoshida and N. Okamoto, “ Nobel Partial Esterification Reaction in Poly(amic acid) and Its Application for Positive-Tone Photosensitive Polyimide Precursor”, Polym. J., 41, 604 (2009)

[7]. N. Yoda and H. Hiramoto, “New Photosensitive High Temperature Polymers for Electronic Applications”, J. Macromol. Sci. Chem., A21, 1641 (1984)

[8]. R. Rubner, H. Ahne, E. Kuhn and G. Kolodziej, “Photopolymer –The Direct Way to Polyimide Patterns-“, Photogr. Sci. Eng., 23, 303 (1979)

Downloaded from http://meridian.allenpress.com/ism/article-pdf/2018/1/000476/2341830/2380-4505-2018_1_000476.pdf by guest on 28 November 2022