Development of Novel Low-temperature Curable Positive-Tone Photosensitive Polyimide with High Elongation

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Recently, progress of semiconductor packaging is drastic and multi-pinned devices such as Fan-out Wafer Level Packages (FOWLPs) attract much attention. For those applications, photosensitive polyimides (PSPIs) are applied as re-distribution layers (RDLs) and they are required to have high level of properties such as adhesion to metal and reliability. We developed novel low-temperature curable positive-tone photosensitive polyimides (posi-PSPIs) with high elongation, strong adhesion to the copper RDLs, and high chemical resistance for establishing the multi RDLs by improving the base-polyimides and incorporating polyimides with cross-linkers and adhesion promoters.

Keywords: polyimides, redistribution layers, photo-sensitive, low temperature curable, high elongation

1. Introduction

As the package size of integrated circuits (ICs) and pin-pitches of the devices dramatically decrease, the integrated multi-layered distribution technologies for IC chips have been developed due to their high performance, low fabrication costs, and miniaturization. Recently, dielectric materials for re-distribution layers (RDLs) have been focused on for the multi-pinned devices such as Fan-out Wafer Level Packages (FOWLPs), which is the one of the latest packaging trends in microelectronics [1-3]. There are a few requirements for dielectric materials as follows: the low-temperature curable nature ($<250\text{ }^{\circ}\text{C}$) because the devices are embedded by the molded compound with low heat resistance, the strong adhesion to the copper RDLs, high chemical resistance, and high reliability in the multi-layered dielectric materials after the reliability test, for instance thermal humidity test, thermal cycle, and high-impact test, and so on [4].

In this study, we have developed the novel low-temperature curable positive-tone photosensitive dielectric materials for RDLs by

using the characteristic pre-imidized PI. Various types of low temperature curable PSPIs named LT series and LT-S series have been released for customer requirements such as low residual stress, high photosensitivity, and high glass transition temperature (T_g). Moreover, the low-temperature curable cross-linkers and the adhesion promoters have been introduced to meet the customer requirements. However, the high-impact resistance of such dielectric materials still remains. In this recent study, the electric materials with high elongation are also described to achieve the high reliability toward the high-impact test because that property can be related to enhancing the durability of materials.

2. Experimental

2.1. Measurement

Number- and weight-average molecular weights (M_n and M_w) were measured by size exclusion chromatography (SEC) on Waters Model 510 equipped with a pump, a UV absorbance detector, and two polystyrene gel columns of TSK Gel α -2500 and TSK Gel α -4000 (TOSOH) based on

a conventional calibration curve using polystyrene standards. *N*-Methylpyrrolidone (NMP) containing 50 mmol L⁻¹ of LiCl and 50 mmol L⁻¹ of H₃PO₄ (40 °C) was used as a carrier solvent at a flow rate of 0.4 mL min⁻¹. FT-IR spectra were measured on a Horiba FT-720 spectrometer. ¹H NMR spectra were recorded with a JEOL JNM-EX270 spectrometer. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA6200 thermal analyzer at a heating rate of 10 °C min⁻¹ for thermogravimetry (TG) and a Seiko EXSTAR 6000 TMA/SS6100 thermal analyzer at a heating rate of 5 °C min⁻¹ for glass transition temperature (*T*_g) and coefficient of thermal expansion (CTE) measurement. Residual stress of cured samples on silicon wafer was evaluated on FLX-3300-T (TOHO) by measuring the curvature radius using a laser at room temperature. Mechanical properties of films such as tensile strength, young's modulus, and elongation were measured on TENSILON at a speed of 5 mm min⁻¹. Electric properties of films such as volume resistance, surface resistance, and breakdown voltage were measured by using LCR meter. To observe the cross-sectional patterns using a scanning electron microscope (SEM) with secondary electrons (FE-SEM S-4800, Hitachi Ltd.), the specimens were treated to Pt/Pd sputtering. Film thickness was measured by STM-802 (Lambda Å, SCREEN). The acceleration tests as reliability tests were carried out by treating the film on the substrate with Temperature and Humidity Chamber (PI-2ST, TABAI ESPEC CORP.) as Thermal Humidity Storage (THS) test and with Thermal Shock Chamber (TSE-11-A, ESPEC CORP.) as Thermal Cycle (TC) test.

2.2. Materials Preparation

PI was obtained by reacting tetracarboxylic dianhydrides with diamines in 20 wt% NMP at 160 °C for 4 hours under N₂ gas flow.

The PSPI varnish sample was prepared by following procedure. The dried PI (3.51 g), diazonaphthoquinone (DNQ, 0.62 g), and cross-linker (0.12 g) were mixed into 5.75 g of γ -butyrolactone (GBL). The solution was filtered through a 0.2 μ m pore poly(tetrafluoroethylene) filter to remove the particles.

2.3. Pattern formation

The varnish sample was coated on an 8-in Si wafer by a spin-coater (ACT-8, Tokyo-Electron). Then, the coated wafer was soft-baked at 120 °C×180 sec on a hot plate

(ACT-8). The film was exposed by an i-line stepper (Nikon, NSR-2005i9C) from 200 mJ cm⁻² to 800 mJ cm⁻². The exposed film was developed by 2.38% tetramethylammonium hydroxide aqueous solution (TMAHaq) at 23 °C. Finally, the PSPI patterned on wafer was cured in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS Co., Ltd) at a condition of 170–250 °C for 60 min under N₂ atmosphere.

2.4. Evaluation method of adhesion

Tape peeling test was carried out to the cured PSPI on copper plated silicon. This test was also conducted after pressure cooker test (PCT) at a condition of 121 °C, 2 atm, and 100%RH (Figure 1). In addition to the peeling test, the observation of the cross-sectional area for copper patterned substrate coating PSPIs was carried out by the treatment of die singulation with a diamond blade, ion milling using a cross-section polisher (Argon ion beam, 6.0 kV, 7 sccm, 7 hrs), and FE-SEM observation, or by the FIB-SEM treatment with the condition of 40 kV for 10 hrs, respectively.

<Classification>

Surface of cross-cut area from which flaking has occurred. (Example for 6 parallel cuts)	None						Greater than 65%
Classification	5	4	3	2	1	0	

Figure 1. Schematic illustration of the tape peeling test for the evaluation of copper adhesion.

2.5. Chemical resistance test

Wafer chips with cured film of patterned PSPI were immersed in various types of solvent for several conditions. The resulting PSPI patterns were evaluated by microscope to clarify the generation of crack or delamination.

3. Results and discussion

3.1. Preparation and Pattern Formation of PSPI

Conventional positive-tone photosensitive polyimide is composed of alkali soluble polyimide precursor and naphthoquinonediazide photosensitive

compound (DNQ) [5]. In the conventional procedure for producing a polyimide, it was required to be heated up to 300 °C to complete imidization, leading to high shrinkage, outgassing, and high residual stress. Therefore, the pre-imidized polyimide was designed to improve such properties (Figure 2). The obtained polyimide, **P1**, is soluble in polar organic solvent such as NMP, dimethyl sulfoxide (DMSO), and GBL at room temperature because of introducing the bulky unit into polyimide backbones by twisting the coplanar imide rings and loosening the packing of the main chain of polymer.

P1 is also soluble in alkaline solution because of phenolic hydroxyl groups introduced into **P1** and it can be patterned by using alkaline developer such as TMAHq with high resolution.

The weight-average molecular weight and polydispersity index of **P1** was determined to be 27,000 and 2.1, respectively. In the FT-IR spectrum of **P1**, the characteristic imide peaks at 1786 (C=O asymmetric stretching), 1722 (C=O symmetric stretching), and 1385 cm⁻¹ (C-N stretching) were assigned, indicating complete imidization. Also, the chemical structure of **P1** was confirmed by ¹H NMR analysis.

Figure 2. The chemical structure of polyimide. X and/or Y: rigid and flexible units.

Next, we observed the pattern shape of **P1** with varnish sample which is the GBL solution of **P1** with DNQ derivatives and thermal cross-linker (**PSPI-1**).

Figure 3 shows the SEM image of the obtained fine pattern.

The resolution of **PSPI-1** is around 5 μm and 70° of the taper angle at a 7 μm film thickness, which could be applicable for the metal sputtering.

Figure 3. The 5 μm line pattern of **PSPI-1**.

3.2. Chemical Resistance

Chemical resistance of the patterned **PSPI-1** was tested by using following solvents: NMP, propylene glycol monomethyl ether acetate (PGMEA), DMSO, acetone, isopropanol (IPA), 1% HFAq, aqueous mixture of H₂SO₄ and H₂O₂ (4/1 w/w), 2.38% TMAHq, and 25% NaOHq. **PSPI-1** showed the high resistance to all solvents above and its pattern have not changed after the test, indicating that the degree of curing is enough for **PSPI-1** and it is suitable as a low temperature curing material.

3.3. Thermal and Mechanical Properties

The thermal properties of **PSPI-1** were evaluated by TG and TMA at the heating ratio of 10 °C min⁻¹ and 5 °C min⁻¹, respectively. **PSPI-1** possessed a relatively high thermal stability over 350 °C (5% weight loss temperature, *T*_{d5%}), and **PSPI-1** showed the glass transition at over 150 °C and about 60 ppm °C⁻¹ of CTE by TMA, which was the relatively high thermal stability among low temperature cured materials. This high thermal stability is attributed to the polyimide backbone and the low temperature curable thermal cross-linker.

3.4. Adhesion to Copper

The adhesion of **PSPI-1** to copper was evaluated by a tape peeling test as shown in Figure 1. **PSPI-1** has high adhesion strength to copper classified with '5' even after the PCT test, indicating that **PSPI-1** is applicable as an insulation layer for RDLs without any delamination between **PSPI-1** and copper layer. The strong adhesion to copper of **PSPI-1** was probably caused by the interaction between the polar imide group and the copper surface [6].

3.5. LT Series

Based on **PSPI-1**, various types of low temperature curable PSPIs were developed for the customer requirements as LT series (Table 1).

3.6. For high reliability

As mentioned in the beginning, high reliability of the multi-layered package is considered when the insulating materials for RDLs are developed. So far, the mechanical property, especially elongation (>40%), is anticipated to be a key factor toward high reliability without generating any crack and breaking RDLs. Hence, we have impr-

Table 1. Physical properties of LT series.

Properties	Cure	LT-6100	LT-6300	LT-6500	LT-6600
Tensile strength / MPa	200 °C	100	110	121	112
Elongation / %	170 °C	30	30	30	30
	200 °C	20	20	20	20
	250 °C	20	20	20	20
Young's modulus/ GPa	200 °C	2.6	2.6	3.4	2.9
CTE/ ppm °C ⁻¹	200 °C	70	61	65	60
Residual stress / Mpa	170 °C	13	13	21	13
	200 °C	13	21	35	20
	250 °C	25	23	39	26
$T_{65\%}$ / °C	200 °C	382	374	393	367
	250 °C	388	380	412	371
T_g (TMA) / °C	200 °C	160	180	232	194
	250 °C	—	201	287	212
Dielectric Constant	200 °C	3.7	3.4	3.1	3.4
Volume resistance/ W cm		>10 ¹⁴	>10 ¹⁴	>10 ¹⁵	>10 ¹⁵
Surface resistance/ W		>10 ¹⁴	>10 ¹⁴	>10 ¹⁵	>10 ¹⁵
Breakdown voltage/ kV mm ⁻¹		>420	395	>420	>420
Water absorption/ %	200 °C	1.7	1.3	1.1	1.6

oved the elongation property of LT-series. The concept of enhancing elongation is shown in Figure 4. The improved polyimide, **P2**, with flexible molecular units in a part of **P1** was introduced to enhance the elongation property of the obtained film, which is assumed to increase the entanglement of each polymer chain.

Figure 4. The design concept for enhancing elongation. (a) Pre-imidized polyimide, P1, (b) P1 with a part of flexible unit, P2.

Fine **PSPI-2** patterns were successfully obtained in the thickness range of 5 to 15 μm . After curing at 220 °C for 60 min, the obtained fine patterns are shown in Figure 5, and mechanical and thermal properties are summarized in Table 2. The obtained **PSPI-2** film exerted the excellent elongation property over two times higher than that of LT-series. It was assumed that the effective entanglement of each polymer chain caused high elongation by introducing flexible unit in the polymer backbone. In addition, thermal humidity

storage (THS) test and thermal cycle (TC) test for **PSPI-2** were demonstrated as quasi-reliability test.

Figure 5. The 5 μm line & space pattern of **PSPI-2**.

Table 2. Mechanical and thermal properties of **PSPI-2**.

Properties	220 °C, 60 min	
	Before THS ^a	After THS ^a
Tensile strength/ MPa	140	135
Elongation/ %	70	70
Young's modulus/ GPa	3.0	3.1
T_g (TMA)/ °C	275	275
CTE/ ppm °C ⁻¹	54	54

^a Thermal humidity storage (THS) test at a condition of JEDEC Level 1. (85 °C, 85%RH 168 hrs)

Figure 6. The top views for **PSPI-2** coating on the copper-pad substrate at a curing condition of 180 °C for 1 hr. (a) Illustration of the structure for **PSPI-2** coated on the copper-pad patterned substrate. (b) After curing, (c) after the 10 times reflow treatment at 270 °C for 1 min, and (d) additional 200 cycle TC test at a condition from -65 to 150 °C after the reflow treatment.

Thermal and mechanical properties of **PSPI-2** have not changed even after THS, meaning the promised reliability in the package system without generating any crack and breaking RDLs. In fact, no crack was observed in the cured film coating on the Cu-pad patterned substrate even after TC test at a condition from -65 to 150 °C (Figure 6).

Chemical resistance of the patterned **PSPI-2**

was also investigated by using several solvents summarized in Table 3. As a result, **PSPI-2** shows the good chemical stability and its pattern have not changed after the treatment to all tested solvent (Figure 7).

Table 3. Chemical resistance for patterned **PSPI-2**.

Solvent	Conditions (Temp. / Time)	Results of thickness change
Acetone	25 °C / 30 min	less than 3%
IPA	25 °C / 30 min	less than 3%
2.38% TMAH _{aq}	25 °C / 30 min	less than 3%
Stripper ^a (DMSO-base)	60 °C / 30 min	less than 10%
NMP	60 °C / 30 min	less than 10%
Flux (water-base)	250 °C / 60 sec	less than 5%
30% H ₂ O ₂	50 °C / 30 min	less than 3%
10% H ₂ SO ₄	25 °C / 30 min	less than 3%
10% H ₃ PO ₄	25 °C / 30 min	less than 3%
2% HFA _{aq}	25 °C / 10 min	less than 3%

Cure condition: 220 °C for 1 h.

^a DMSO (67–73%)+NMP (15–25%)+organic amine (3.5–4.5%)

Figure 7. Optical microscope images of patterned **PSPI-2** (a) before/(b) after the treatment with a DMSO-based stripper.

Next, the adhesion of **PSPI-2** to copper was evaluated by a tape peeling test, and **PSPI-2** possesses enough high adhesion strength to copper no less than LT series, classified with '5' even after the PCT test.

Moreover, in order to evaluate the more precise copper adhesion of **PSPI-2**, the observation of the cross-sectional area for **PSPI-2** coated on the copper patterned substrate as shown in Figure 8. Before the observation of the cross-sectional area, the fabrication of specimens is necessary to obtain clear images. There are a few methods to fabricate them as follow. One is the continuous fabrication of polishing and observation by applying FIB-SEM. The other is polishing the cross-sectional area by ion beam using argon to achieve a flat

cross-sectional area after roughly cutting the specimen, and then the processed cross-sectional area can be observed by FE-SEM. Figure 9 shows the processed specimen by FIB-SEM and its magnification image. The well adhesion of **PSPI-2** to the copper surface was apparently observed as shown in Figure 9. As a result, no delamination between **PSPI-2** and copper occurred, meaning high adhesion property to copper RDLs.

Electronic property of **PSPI-2** was also investigated by applying the voltage to the copper patterned substrate as a copper migration test (Figure 10). The result indicates that the reliability of **PSPI-2** is quite high because of keeping the resistivity even after THS test at a condition of 130 °C/85RH%/196 hrs/10 V.

Figure 8. Illustration of the structure for **PSPI-2** coated on the copper patterned substrate.

Figure 9. SEM images of the cross-sectional areas for the (a) overall view of **PSPI-2** after the FIB treatment at a condition of 40 kV for 10 hours, and (b) the magnified one.

Based on **PSPI-2**, novel low temperature curable positive-tone photosensitive dielectric materials with high elongation were developed as LT-S series, named LT-S8000s.

In the course of this study, it was found that LT series and LT-S series had high sensitivity, good chemical resistance, excellent copper adhesion, and high elongation which are desirable to achieve the promised reliability as RDL dielectric materials, especially for FOWLPS.

Figure 10. Resistivity of **PSPI-2** cured for 220 °C for 1 hour during the treatment at a condition of 130 °C, 85RH%, and 10V bias for 196 hrs.

4. Conclusion

We have developed the novel low-temperature curable positive-tone photosensitive dielectric materials for RDLs by using the characteristic pre-imidized PI. Various types of low temperature curable PSPIs named as LT series show low residual stress, high photosensitivity, excellent adhesion to copper, and high T_g up to 230 °C for customer requirements.

We have also developed the novel low-temperature curable positive-tone photosensitive dielectric materials with the high elongation property for RDLs, named as LT-S series. The high elongation concept contains the introduction of the flexible molecular unit in the base polymer backbone, which is assumed to increase the entanglement of each polymer chain. As a result, the composition based on the above polymer and the conventional low-temperature curable cross-linkers cured at below 250 °C show the high elongation property up to 70%. In addition, the pattern fabrication process of the developed dielectric material was carried out, and the fine patterns were obtained with high resolution and high sensitivity developed by 2.38% TMAHaq

solution as an alkaline developer. Moreover, the obtained patterned material possesses high chemical resistance toward the DMSO-based resist stripper, and the excellent adhesion to copper and the constant resistivity after the quasi-reliability test. This material is expected to be a key material by contributing to enhance the next-generation semiconductor device packaging reliability.

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