Low Stress and Low Temperature Curable Photosensitive Polyimide

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Low stress / low temperature curable photosensitive polyimide (PSPI) with excellent reliability during thermal cycle (TC) has been developed for a quite some time. The effect of residual stress concerning PSPI on copper-PSPI inter-connect structure was examined by Finite Element Method (FEM), and it became evident that the crack has tendency to appear at the top corner between copper and PSPI, where highest stress lay during the cooling process of TC test. Low stress PSPI is one of the candidates to reduce residual stress on copper-PSPI inter-connect structure, and indeed, no crack was found after FEM and TC test. Through a series of tests mentioned above, we came to realize that an introduction of soft segment into polyimide backbone of PSPI is the key factor to create a robust low stress PSPI. In addition of creating a robust low stress / low temperature curable PSPI, further research was conducted to improve the copper compatibility of PSPI through grasping the ways of controlling the oxidation of copper.

Keywords: Photosensitive polyimide, Low stress, Finite element method, Reliability

1. Introduction

Recently, higher density, narrower bump pitch and thinning of 3D Jisso are the trends in the advanced integrated packages. Moreover, in order to implement the trends of advanced integrated packages, an application processor (AP) controlling all functions of mobile devices is believed to be one of the key devices to do so. Thus far, most APs are integrated by Package on Package (PoP) technology, which includes considerable thick substrate for mounting devices [1]. In the recent package trend, Fan-Out Wafer Level Package (FO-WLP) technology became a remarkable package technology, which opened-up a technological window to manufacture extremely thin devices [2]. The FO packages are usually composed of semiconductor die placed in mold resin and redistribution layer (RDL) fabricated on the top of semiconductor die, within mold resin. RDL patterns consist of conductive copper metal and non-conductive insulant materials such as photosensitive polyimide (PSPI) and polybenzoxazole (PSBPO) to insure package reliability. When selecting non-conductive low temperature curable materials, there are several critical requirements to prevent damages to the FO-WLP packages, and one of the requirements is the curing temperature. Selection can easily be fulfilled if robust conventional PSPI and PSBPO, which require high temperature treatment to complete the ring closure reaction; however, FO-WLP require low temperature cure. It is widely known that to complete low temperature ring closure reaction for PBO precursor, introduction of flexible structure in polymer chain worked successfully [3,4]. On the same note, report has indicated that PBO ring closure reaction was accelerated by adding sulfonic acid and photo base generator during low temperature imidization [5,6]. A phenomenon of applying additives to PSPI was also reported by Sasaki [6], which made the development of low temperature curable PSPI for RDL insulator of FO-WLP.

We have developed various type of PSPI materials for several electronic devices such as semiconductor and OLED. A PSPI composed of novel partially esterified poly (amic acid) and...
diazonaphthoquinone compound was developed by utilizing photosensitive polymer technologies [7,8]. However, the problem with this polymer technology was that curing temperature over 300 °C necessitated the conversion of poly (amic acid) to polyimide by intermolecular cyclization. For FO-WLP applications, low temperature curable PSPIs were required due to low thermal stability of mold compound and memory device as mentioned before. In addition, copper compatibility and mechanical reliability of PSPI are also important because the FO-WLP technology requires to form copper RDL with PSPI as an insulator.

In this report, the development of low temperature curable PSPI by utilizing a pre-imidized polyimide with low temperature curable cross-linker will be introduced. We have investigated our own development through a series of demonstrative stress simulation of quasi FO-WLP package by changing physical parameters of PSPI by FEM as well as the effect of residual stress of PSPI when utilized for RDL insulators. Furthermore, we have also focused our study to implement copper compatibility to the reliability of PSPI.

2. Experimental

Materials. PI was synthesized by polycondensation of tetracarboxylic dianhydrides with diamines. The proper amount of diamines was placed in a 4-neck flask with a mechanical stirrer, thermometer, and nitrogen inlet. Then, N-methyl-2-pyrridone (NMP) was added to the flask. The flask was heated to 60 °C under nitrogen flow. After diamines have dissolved, the proper amount of tetracarboxylic dianhydrides was added into the diamine solution. The mixture was stirred for an hour at 60 °C, then heated to 180 °C. Polycondensation reaction was carried out at 180 °C for 4 hours. After cooling to room temperature, PI solution was poured into the water to precipitate. The obtained PI was collected by filtration, then dried at 50 °C for 72 hours in a convection oven.

PSPI varnish sample was prepared by following procedure. The dried PI (3.51g), diazonaphthoquinone compound (DNQ, 0.62g), and cross-linker (0.12g) were mixed into 5.75 g of γ-butyrolactone (GBL). The solution was filtered through a 0.2 μm pore poly (tetrafluoroethylene) filter to remove the particles. Chemical structures of DNQ and cross-linkers are shown in Fig. 1.

Pattern formation. The obtained varnish sample was coated on an 8-inch Si wafer by a spin-coater (ACT-8, Tokyo Electron), then soft-baked at 120 °C for 3 min on a hot plate equipped with ACT-8. The film was exposed by an i-line stepper (Nikon, NSR-2205i14) from 200 mJ cm−2 to 800 mJ cm−2. After lithographic exposure, the exposed film was developed by 2.38% tetramethylammonium hydroxide aqueous solution (TMAHaq) at 23 °C. Finally, the 5–15 μm PSPI patterned wafer was obtained after cured in a clean oven (CLH-21CD (V)-S, KOYO THERMOSYSTEMS Co., Ltd) at a condition of 180–250 °C.

Measurement. Number- and weight-average molecular weights (Mn and Mw) were evaluated by size exclusion chromatography (SEC) on Waters Alliance e2695 equipped with following features: pump, 2489 UV/Vis detector, 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 (50 °C) was used as a carrier solvent at a flow rate of 0.4 mL min−1. 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). Seiko EXSTAR 6000 TMA/SS6100 thermal analyzer was also used at a heating rate of 5 °C min−1 for glass transition temperature (Tg) 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. To observe the cross-sectional patterns using a scanning electron microscope (SEM) with secondary electrons (FE-SEM S4800, Hitachi Ltd.), the specimens were treated to Pt/Pd sputtering. Film thickness was measured by STM-802 (Lambda Å, SCREEN). The accelerative 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, with a convection oven for High Temperature Storage (HTS) test, and with Thermal Shock Chamber (TSE-11-A, ESPEC CORP.) as Thermal Cycle (TC) test, respectively. Copper migration test was conducted by using copper patterned substrate (Line and Space, 2/2 μm) stored in thermal and humidity chamber with 3.3 V bias. Abaqua 2018.HF3 was applied to carry out stress simulation of FO-WLP model by FEM.

3. Results and discussion
3.1. Stress simulation by FEM

Stress simulation was carried out by Abaqua 2018.HF3 with quasi FO-WLP structure as shown in Fig. 2, and material parameters are summarized in Table 1.

Fig. 3 shows that a single layer RDL stress simulation with parameters of Polyimide A during TC test. The highest stress was observed at the top corner between copper and polyimide, especially during cooling process of TC test. From this data, it is safe to say that crack during TC test may be occurring at high stressed regions.

Table 1. Material parameters for FEM simulation.

| Material     | Modulus (GPa) | Poisson Ratio | CTE (ppm K⁻¹) |
|--------------|---------------|---------------|----------------|
| Polyimide A  | 3.2 ± 0.40    | 0.35          | 40.2 ± 5.9     |
| Polyimide B  | 3.0 ± 0.40    | 0.35          | 39.9 ± 6.2     |
| Ti / Cu      | 6.8 ± 0.40    | 0.35          | 48.1 ± 6.5     |
| Cu           | 11.0 ± 0.40   | 0.34          | 14.8 ± 6.6     |
| Ni           | 7.0 ± 0.40    | 0.31          | 11.3 ± 7.7     |
| Solder (Sn)  | 5.0 ± 0.50    | 0.36          | 26.8 ± 6.4     |
| Si substrate | 3.8 ± 0.20    | 0.28          | 1.7 ± 2.6      |

Fig. 3. Stress simulation results by FEM during TC test at −55°C and 125°C.

Fig. 4. Stress simulation results by FEM applying for multi layered model during TC test at −55°C.

Moreover, the influence of the number of the RDL layer verses occurrence of crack to the package stress simulation was also investigated. When comparing 2 layer structure to 4 layer structure, 4 layer structure showed rather high stress at the top corner between copper and PI (Fig. 4). In order to prove this phenomenon, comparative data between Polyimide A and Polyimide B revealed the answer. These particular results showed Polyimide B with lower modulus than that of Polyimide A showed decreased stress at the corner between copper and PI even in multi layered structure. Therefore, low modulus PI can be considered to effectively...
suppress or release the package stress, which is expected to enhance the durability for reliability test.

Fig. 5. The schematic model of low modulus PI.  

3.2. Development of photosensitive polyimide with high reliability

According to FEM simulation results, low modulus PI (Polyimide B) is one of the suitable materials for making the stress between copper and PI lower. We designed PI backbone with special soft segment as shown in Fig. 5. The coating material of the obtained PI with soft segment containing DNQ, cross-linker and other ingredients has low modulus nature (1.7 GPa). Furthermore, low residual stress including alkaline solubility and fine PSPI patterns were successfully obtained even at the thickness range of 5 to 15 µm. Basic properties are summarized in Table 2. Newly developed PSPI shows high thermal stability, mechanical property and high sensitivity in addition to low modulus and stress nature. Fig. 6 shows the SEM images of the fine patterns. The resolution of PSPI is around 5 µm and 10 µm at a 7 µm film thickness, which could be applicable for the metal sputtering.

Table 2. General properties for PSPIs.

| Properties                     | Measurement Method | Previous Type | Newly Developed |
|--------------------------------|--------------------|---------------|-----------------|
| Curing Condition               | °C/min Oven        | 200/60        | 230/60          |
| Tensile strength (MPa)         | Tensile Test       | 135           | 120             |
| Elongation (%)                 | Tensile Test       | 65            | 100             |
| Young’s modulus (GPa)          | Tensile Test       | 2.1           | 1.7             |
| CTE (ppm/°C)                  | TMA                | 60            | 55              |
| Residual stress (MPa)          | Bending Test       | 28            | 20              |
| 5% weight loss temp. (T5)      | °C TGA             | 340           | 340             |
| Volume resistance (Ωcm)        | LCR meter          | 1.0x10¹⁰      | 1.0x10¹⁰        |
| Surface resistance (Ω/s)       | LCR meter          | 1.0x10¹⁰      | 1.0x10¹⁰        |
| Photo sensitivity (mJ/cm²)     | i-line stepper     | 300           | 400             |
| Water Absorption (%)           | TGA                | 1.0           | 0.8             |

3.3. Reliability and copper compatibility of photosensitive polyimide

Reliability tests for the newly developed PSPI with low modulus and low residual stress included TC test, HTS test, and copper migration test. The condition for TC-B test was 1000 cycles at –55 °C to 125 °C. The result of this reliability test was successful, which resulted with no crack.

The other issue regarding reliability is the delamination between copper and PSPI during HTS. Although there is no delamination after cure, delamination and void build-up tend to occur during and after HTS at a condition of 150 °C for 1000 hours. Through a detailed observation by SEM, the interface where delamination and void build-up doesn’t occur between copper and PI, rather it occur between copper and copper oxide layers (Fig. 7 a)). Fig. 7 b) shows the interface by secondary ion mass spectrometry (SIMS) to understand the changes during HTS. Horizontal axis is the depth of copper and PI layers and vertical axis is the detection intensity of various elements. After curing, copper oxide was not formed because curing condition was inert. However, copper oxide was generated after HTS. This result indicates diffusion of copper ion into polyimide and oxidation of copper is taking place during HTS. Therefore, in order to prevent copper oxidation, an introduction of anti-copper oxidant into newly developed PSPI was necessary to suppress copper oxidation. Evidently, when we introduced an anti-copper oxidants into our newly developed PSPI, it successfully suppressed the growth of copper oxide and the diffusion of copper ion.

Fig. 6. Cross-sectional view of via patterns for newly developed PSPI.

Fig. 7. a) Cross-sectional view of the test vehicle, b) SIMS analysis before/after HTS.
Finally, the insulation property of PSPI called copper migration was investigated by bias HAST with 2 μm line and space copper electrode. The result indicates that the reliability of PSPI is quite high because of its ability to keep the resistivity even after THS test at a condition of 130 °C, 85%RH and 3.3 V for 300 hours (Fig. 8).

Fig. 8. The result of copper migration test under bias HAST condition (2 μm line and space copper electrode, 130 °C, 85%RH and 3.3 V for 300 hours).

4. Conclusion

We have investigated the stress effect of polyimide on copper multi-layer structures by FEM simulation. Polyimide designed with soft segment which has low modulus and low residual stress tends to decrease the stress at the corner between copper and PI even in multi layered structure.

The result of PSPI composition based on PI with soft segment when utilized on quasi FO-WLP structure showed promising durability result without crack after TC-B test. In addition, delamination between copper and copper oxide can be successfully suppressed by introducing anti-copper oxidant into PSPI. Moreover, newly developed PSPI showed excellent insulation property investigated by bias HAST using 2 μm line and space copper electrode.

This material is expected to make huge impact and contributions to enhance the reliability of advanced semiconductor packaging.

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