Low Temperature Curable Polyimide for Advanced Package

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Advanced packaging technology requires low temperature curable and low residual stress material as dielectric layer. We developed appropriate product based on our previous study and so on. As a result, we used polyimide structure with acidity control of amine unit techniques for polymer and additive A for copper adhesive. And we also evaluated the product regarding various items.

Keywords: polyimide, photosensitive, low temperature curable, low residual stress

1. Introduction

For long years, the progress of semiconductor devices has been achieved in accordance with Moore’s law, namely miniaturization. But recently, it needs very complicated techniques, so performance and productivity are gradually hard to compatible. Therefore the packaging technology is paid attention and many types of advanced packaging are actively developed. Particularly, Fan-Out Wafer Level Package and Through Silicone Via are considered to be the future mainstream. Because those packaging techniques are possible to achieve high I/O, superior electrical performance, low energy consumption and small form factor. Both packaging techniques use low thermal stability materials within the structure or during production process. So, they need low temperature curable polymer materials as their dielectric layer. And now, almost every semiconductor devices are required to be thin, especially for mobile application. So, many chips are becoming thinner and thinner, and the bending of chips and wafer are concerned. Accordingly, low internal stress also required for dielectric layer materials.

As dielectric layer materials, polyimide and polybenzoxazole are widely used, because of its excellent heat resistance, chemical resistance, and high mechanical properties [1]. In our previous study, we showed polyimide is more suitable than polybenzoxazole from reliability for thermal cycle test viewpoint by experiment and finite element analysis (FEA) because of its good elongation at -55deg.C and the fatigue properties [2,3]. On the other hand, we also reported it was necessary to choose appropriate thickness and modulus to work as stress buffer at drop test by FEA [4].

In consideration of these information, we showed our solution of dielectric layer materials for advanced package in this article.

2. Experimental

2.1. Synthesis of polyimide precursor

Tetracarboxylic acid dianhydride, pyridine and alcohol which is introduced to side chain of polyimide precursor were dissolved into γ-butyrolactone (GBL), and the solution was stirred at room temperature for 16 hr. Then, the solution was cooled with ice bath, GBL solution of N,N'-dicyclohexylcarbodiimide was added to the solution. Subsequently, diamine in GBL was added to the solution. The solution was stirred at room temperature for 2 hours. After that, The solution was filtered to remove N,N'-dicyclohexylurea as a by-product and poured into a large amount of water. The polymer precipitate was filtrated and dried at 40 °C for 72 hours under vacuum.

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The molecular weight of polyimide precursor was measured by gel permeation chromatography (GPC).

2.2. GPC measurement
0.02g of polymer was added to 5mL N-methyl pyrrolidone (NMP). GPC measurement of each sample was performed with the analytical curve of standard polystyrene.

2.3. Preparation of photosensitive polyimide precursor composition
Photosensitive polyimide precursor varnishes were prepared by adding the polyimide precursors, photo-initiators, crosslinking agents, and adhesion promoters to NMP. The solution was filtered by 1.0um pore PTFE filter.

2.4. Lithography and observation
Photosensitive polyimide precursor varnishes were coated on 6 inch silicon wafer and pre-baked at 100 °C for 4 minutes (Mark-8, Tokyo Electron). The coated film about 14 μm thickness on wafer was exposed through a patterning mask by i-line stepper (NSR2005i8A, Nikon) from 100 mJ/cm² to 800 mJ/cm². The exposed film was developed with cyclopentanone and then rinsed with 2-propylene glycol-1-methyl ether acetate by a spray development (SC-W60A-AV9, SOKUDO). The patterned film was observed by optical microscope.

2.5. Curing
Pre-baked or post-developed film on wafer was cured under nitrogen atmosphere (VF-2000B, Koyo Thermo System).

2.6. FT-IR measurement
Cured film on wafer was measured by ATR method (Nicolet 380, Thermo Scientific).

2.7. Measurement of elongation, strength and Young’s modulus
7-μm thickness of cured film was measured by the tensile testing machine (Tensilon UTM-II-20, Orintec).

2.8. Measurement of thermal properties
5% weight loss of cured film was measured by thermogravimetric analysis (TGA50, Shimadzu). Glass transition temperature (Tg) and coefficient of thermal expansion (CTE) of cured film was measured by thermomechanical analysis (TMA50, Shimadzu).

2.9. Measurement of residual stress
Bending amount of bare 6 inch wafer was measured by film stress measurement system (FLX-2320, KLA-Tencor). Then, photosensitive polyimide precursor varnish was coated on the wafer and cured. Bending amount of the wafer with cured film was measured same as above and residual stress was calculated with bending amount data of bare wafer.

2.10. Chemical resistance
Patterned and cured film was treated with photo resist stripper, metal etchants and flux. In the cases of photoresist stripper and metal etchant, cured film on wafer was immersed in these chemicals under each condition. The tested film on wafer was rinsed by deionized water for 5 minutes and then dried at room temperature. As for flux resistance, the flux was put on cured film on wafer and it was passed through reflow oven under nitrogen atmosphere. The maximum temperature in the reflow oven was 260 °C. Then the sample was rinsed by deionized water for WS-600, by PineAlfa ST-100SX and deionized water for R5003 and dried. Appearance after the test was observed by optical microscope. Thickness change after the test was measured by contact film thickness measuring apparatus.

2.11. Adhesion
Cured film on various substrate wafer was prepared. And stud with epoxy resin was adhered by heating with 150 °C for 90 min to the surface of the cured film. This sample was measured by universal materials tester (ROMULUS IV, Quad group).

3. Results and discussion
3.1. Design concept of PIMEL™ BL-301
One of the requirements to be ‘low temperature curable polyimide’ is completing the imidization at low temperature cure. Because the excellent mechanical and thermal properties of polyimide come from polyimide structure itself, not precursor. Imidization usually occurs with high temperature, i.e. over 300 °C. And many approach to imidization with low temperature were known. For example, adding basic catalyst or plasticizer, using flexible unit or difficult to rotate unit as polymer backbone and so on. But
these methods are apt to gather undesirable side effects. Therefore, we selected another means, that is to control the acidity of amine unit of polyimide precursor.

On the other hand, good adhesion to copper is very important for re-distribution layer materials. Because almost every re-distribution metal is copper. We studied and found the additive A to improve the adhesion to copper.

As a result, we have developed low temperature curable polyimide product PIMEL™ BL-301 with referring to all the above information. In the following section, various types of evaluation of PIMEL™ BL-301 with low temperature cure and high temperature cure condition are described.

3.2. Evaluation of imidization
We measured the degree of imidization of PIMEL™ BL-301 by FT-IR. We defined ‘Imide index’ as following equation.

\[
\text{Imide index} = \frac{\text{Absorbance (1380 cm}^{-1})}{\text{Absorbance (1300 cm}^{-1})}
\]

![Figure 1. Imide index of PIMEL™ BL-301.](image)

As shown in Figure 1, imide index of PIMEL™ BL-301 is same and saturated in the range between 190 and 300 °C cure. It indicatesimidization of this product already completes in 190 °C cure condition. This result tells our strategy to achieve imidization at low temperature cure condition is correct.

3.3. Evaluation of cured film properties
Table 1 shows thermal and mechanical properties of PIMEL™ BL-301. Even low temperature cure condition, this product shows excellent and almost same mechanical properties as high temperature, except for residual stress. It also indicates PIMELTM BL-301 can be used sufficiently above 200 °C cure condition. And its modulus value is appropriate for the target we set.

Thermal properties changed in accordance with cure temperature and it leads to residual stress value change.

3.4. Evaluation of chemical resistance
We tested chemical resistance of PIMEL™ BL-301. The chemicals we tested are ST-44 (ATMI Inc.), Acetone, PGME and NMP as photoresist stripper, 30% Nitric acid aq., 30% sulfuric acid aq. and 1% HF aq. as metal etchant, WS-600 (Alpha Metals Japan) and R5003 (Cookson Electronics Co. Ltd) as flux. Flux resistance was done by 260 °C reflow condition. We made judgment by pattern inspection, thickness measurement and so on.

PIMEL™ BL-301 shows excellent chemical resistance even low temperature cure as Table 2. These properties are enough to apply for re-distribution layer.

3.5 Evaluation of adhesion
We evaluated adhesion of cured PIMEL™ BL-301 to various substrate by stud-pull test method. We only showed the results of after PCT treatment in Table 3. In the table, ‘>70 MPa’ means over limitation of the measurement due to breakage of the epoxy adhesive between cured film and stud. In all cure condition, there is no
problem at all. And it goes without saying that adhesion without PCT is also excellent.

Table 3. Adhesions of PIMEL™ BL-301 to various substrates.

| Substrate | 200deg.C | 250deg.C | 300deg.C |
|-----------|----------|----------|----------|
| Si        | > 70 MPa | > 70 MPa | > 70 MPa |
| SiN       | > 70 MPa | > 70 MPa | > 70 MPa |
| SiO       | > 70 MPa | > 70 MPa | > 70 MPa |
| Cu        | > 70 MPa | > 70 MPa | > 70 MPa |
| Al        | > 70 MPa | > 70 MPa | > 70 MPa |
| PI        | > 70 MPa | > 70 MPa | > 70 MPa |

Table 4. The effect of additive A for adhesion to copper after HTS treatment.

| Substrate | Additive A |               |
|-----------|------------|---------------|
| Cu        | No         | 40 MPa        |
|           | Yes (PIMEL™ BL-301) | > 70 MPa     |

As we described above, adhesion to copper is especially important in re-distribution application and found additive A to improve it. We indicated the effect of additive A by stud pull test after HTS (high temperature storage) treatment at harder condition (175°C, 270 hr) than general in Table 4. Without additive A, adhesion measurement value is low and delamination between cured film and copper is observed. On the other hand, with additive A (i.e. PIMEL™ BL-301) shows excellent adhesion to copper.

4. Conclusion

We have developed low temperature curable photosensitive polyimide precursor product successfully as PIMEL™ BL-301. This product showed low temperature curability (i.e. ability of imidization at low temperature cure), excellent mechanical and thermal properties, chemical resistance and adhesion to various substrate including copper. Furthermore, it can be also used at high temperature cure condition. Namely, PIMEL™ BL-301 is wide cure temperature margin product. We believe this product will satisfy the demand for advanced package dielectric layers.

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