Development of Positive Working Photosensitive Polyimide Coatings for Semiconductor Packages

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This paper describes an approach to develop a positive working photosensitive polyimide coating (positive-PSPI) for semiconductor packages. We designed a new polyimide back-bone for positive-PSPI from a point of solubility, adhesion to molding compound and copper migration. In addition, we found effective adhesion improvers for Cu. From these experimental results, we succeed to develop new positive-PSPI coatings which are suitable for wafer level chip size packaging, bumping protection, as well as buffer coating.

Keywords: photosensitive polyimide, chemical resistance, adhesion, molding compound, silicon, copper, migration

1. Introduction

Electronic device has been progressed to be smaller size, multi-function, and higher operating speed. In order to meet these trends, a flip chip package, which is connected to substrate through the bump directly, is one of the good candidates [1]. For this application, a bump protecting layer is desired to protect device from out-side stress.

On the other hand, WL-CSP (Wafer Level Chip Scale Package) technology as another new solution for small size packaging technology, whose package size is shrinked to a chip scale, has been thought to be applied to many devices [2]. The technology is composed of solder bump formation and reliable inter-dielectric layer formation for rerouting.

![Figure 1. Structure example of WL-CSP](image)

It was required that the material for the inter-dielectric layer has excellent electronic properties, good adhesion to metals, silicon substrates as well as molding compound, chemical resistance, heat stability, and photo-lithographic patterning property because sputtering, plating, and chemical etching technique are applied to make it.

Polyimide have been noted as one of candidates for materials of the dielectric layer and the bump protection because polyimide has been applied for buffer coatings of the semiconductor devices and interlayer of multi-layer circuit board in terms of its good heat resistance and chemical resistance. Especially positive-PSPI has been not only very useful to simplify the polyimide patterning process but also suitable to obtain fine polyimide patterns on the semiconductor chips.

We have developed positive photosensitive polyimide coatings for semiconductor and dielectrics for organic electro-luminescence display applications [3-5].

In this paper, we describe a designing concept of coatings from the point of adhesion to molding compound and metal, as well as adhesion to substrates.

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2. Experimental

2.1 Materials

All compounds and solvents were purchased and provided from chemical manufacturers and used for experiments without further purification.

2.2 Measurement to adhesion to molding compound

(1) A polyimide was coated on a silicon wafer by using a spinner to get 2µm thickness. Heat treatment was carried out at 80°C, 200°C, 300°C and 350°C for 30min. successively in nitrogen.

(2) A glass-fiber reinforced silicone rubber with 4mm diameter holes is put on a polyimide-coated wafer which is heated at 170°C on a hot plate. Molding compound powder was added into these holes and molded under a 5kg weight at this temperature for 5min. The sample was treated at fixed temperature for fixed time for post curing of the molding compound.

(3) Then the sample was treated under saturated vapor pressure of water at 121C for 168hrs.

(4) Measure the adhesive strength of the sample by Tensionl RTM-10 (Orientech Corp.) with special adaptor at a speed of 5mm/min.

2.3 Measurement of Dynamic visco-elasticity

(1) A polyimide was coated on a silicon wafer by using a spinner to get 10µm thickness. Heat treatment was carried out at 80°C, 200°C, 300°C and 350°C for 30min. successively in nitrogen. A polyimide was coated on a silicon wafer by using a spinner to get 2micrometer thickness. Heat treatment was carried out at 80°C, 200°C, 300°C and 350°C for 30min. successively.

(2) The polyimide film was measured with Rheo-vibron DDV-2EA (Orientech Corp.) from –150°C to 350°C at a heating rate of 2°C/min at 110Hz.

2.4 Cu migration evaluation

The polymer solutions were prepared and spin-coated on the Cu sputtered 4-inch silicon wafers which were pre-baked on a hotplate at 120°C for 3 minutes. The pre-baked wafers were cured at 350°C for 1 hour in a nitrogen purged oven (Koyo-thermosystem INH-21CD). Cu migration was observed by transmission electron microscope (TEM) (Hitachi H-7100FA).

2.5 Chemical resistance evaluation

A polyimide was coated on a silicon wafer by using a spinner to get 5µm thickness. Heat treatment was carried out at 120°C for 3min by a hot plate, and 170°C for 30min and 350°C for 60min successively in the nitrogen purged oven as described above.

2.6 Pattern profile evaluation

Positive-PSPI solutions were prepared, spin-coated and pre-baked by the above condition. Then, coated wafers were exposed by i-line stepper (500mJ/cm²) and developed by a tetra methyl ammonium hydroxide (TMAH) aqueous stepper solution (2.38 wt%) for 90 seconds. The developed wafers were cured under the above condition. The pattern profile was evaluated by scanning electron microscopy (SEM) (Hitachi S-2300).

2.7 Adhesion evaluation to substrates and metals

Coating solutions were spin on various substrates and cured under the above condition. Adhesion between cured film and various substrates was determined by a cross cut method (Scotch tapeB method) (JIS K 5400) after pressure cooker test (PCT) treatment condition whose are 121C, 2.0x10³Pa (2.0atm), and 100%RH (Tabai EHS-211MD).

2.8 Adhesion evaluation to substrates by HF

Coating solutions were spin on Si wafers and cured under the above condition. Cured wafer was treated by 1% HF solution. After the HF treatment, interface between polyimide and Si wafer was observed by SEM.

3. Result and discussion

3.1 Polymer design

One of the photosensitive polyimide coatings is composed of polyimide precursor and naphthoquinone diazide compound (NQD) which is popular in positive novolak photo-resist [6,7]. On the other hand, positive tone photosensitive heat stable coatings were composed of polybenzoxazole and NQD [8,9]. Poly(amic acid) i.e. polyimide precursor has many carboxylic acid groups in a polymer chain. So the alkaline solution solubility is too high due to those carboxylic acids. This fact means that mixture of poly(amic acid) and NQD is still alkaline soluble. To obtain good positive polyimide pattern is hard to achieve. We have developed a new polyimide precursor suitable for the positive tone photosensitive polyimide.
3.2 Visco-elastic properties of polyimides

Adhesion to molding compound is an important factor to obtain high reliable semiconductor. When we found a delamination between polyimide and molding compound due to poor adhesion, we observe a package crack or passivation crack after soldering process. Delamination example photo is shown in Fig.2 by SAT(Scanning Acoustic Tomograph). And package crack example is shown in Fig.3.

**Fig.2 Delamination example of package by SAT (Scanning Acoustic Tomograph)**

**Fig.3 Package Crack picture**

Measured example of polyimide visco-elasticity is shown in Fig.4. As you see the figure, there are 3 relaxations observed. The highest temperature relaxation (200-400C) is called α-relaxation corresponds to glass transition temperature of the polyimide. The second relaxation (100 to 200C) is called β-relaxation(Tβ). The last (lowest) relaxation is called γ-relaxation(Tγ). Greenbun et al. reported that the Tγ originates from small clusters of water which exists in the polyimide film[10]. Cheng et al. reported the Tγ corresponds to n-flipping motions of the phenoxy group[11]. Origin of Tβ is thought to be inter plain slippage of crystalline region by Ikeda et al[12]. Chneg et al. reported that the Tβ corresponds to molecular group motion mainly connected to the dianhydride moiety[11]. Sun et al. reported that Tβ has related to rotation of rigid segment of p-phenylene and imide groups[13]. Recently, Bas et al. concluded that Tβ is related to dianhydride flexibility as well as para- or meta-diame links[14]. As these discussions, Tβ is originated from the large part of polyimide main chain.

**Fig.4 Visco-elastic properties of polyimide**

![DMA curve of polyimide](image_url)

3.3 Adhesion to molding compound

We found that adhesion between polyimide and molding compound dominates by β-relaxation peak temperature of the polyimide[15]. Because the relaxation temperature is close to the post curing temperature of molding compound, interfacial stress between polyimide and molding may relieve by the β-relaxation of polyimide during the post curing. Figure 5 plots the β-relaxation peak temperature vs. adhesion strength. When the β-relaxation peak temperature of the polyimide is lower than the post curing temperature, the adhesion is well. And when the β-relaxation peak temperature of the polyimide is higher than the post curing temperature, poor adhesion was observed.

**Fig.5 Adhesion dependence on Tβ temperature of polyimides**

![Adhesive strength vs Tβ](image_url)
3.3 Adhesion to Si substrate

In order to improve adhesion to Si substrates, aluminum chelate[16], silane coupling agent[17], and silicone diamine co-polymerizing[18] are applied. Adhesion to Si substrate will be more important in near future. Because I/O pin number increases at a tremendous rate, bonding pad space will become narrower to few μm-scale especially for logic LSI[19]. So polyimide width will be few-μm. It is too narrow to keep good adhesion during back-gliding process of LSI.

To investigate the adhesion between polyimide and substrate, cross-cut test (Scotch tape test) was used. This method is a convenient to do, but could not tell the smaller feature size adhesion. We developed adhesion evaluation method instead of the Scotch Tape test. Namely, we observed the interface after diluted HF treatment by SEM.

Before the diluted HF treatment, we do not find any delamination from the Si substrate (Fig.6 Left). When conventional adhesive improvement polyimide coating is used, side-etch at the polyimide-Si interface is observed (Fig.6 Center). We developed new excellent adhesion improvement technique to Si substrate. “PW-1200” and “PW-1500” are shown no delamination, even though those are treated 10min. in the diluted HF (fig.6 Right). Those excellent adhesive coatings endow high reliability to future semiconductors.

![Image of TEM photograph of polyimide on Cu substrate](image)

**Figure 7. TEM photograph of polyimide on Cu substrate**

**Left:** poly(amic acid), **Right:** New polyimide precursor

In order to improve adhesion between polyimide and Cu, we investigated many chemicals which include benztriazole and phenanthroline. Benztriazole and phenanthroline are famous to form a complex with Cu and to protect Cu surface. Unfortunately, benztriazole and phenanthroline were not effective for adhesion in our result. From this investigation, we find an effective compound to improve the adhesion to Cu.

<table>
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<tr>
<th>Cu migration and adhesion results</th>
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<tbody>
<tr>
<td>Migration</td>
</tr>
<tr>
<td>Poly(amic acid) (Kapton type)</td>
</tr>
<tr>
<td>New precursor</td>
</tr>
<tr>
<td>Poly(amic acid) + benztriazole</td>
</tr>
<tr>
<td>New precursor + benztriazole</td>
</tr>
<tr>
<td>New precursor + phenanthroline</td>
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<tr>
<td>New precursor + new compound</td>
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3.4 Cu migration and adhesion

Recently, Cu wiring is much popular in LSI due to its low resistivity [19]. In case of Cr, Ti, or Al, chemical bonding is observed between polyimide and metals. So polyimide exhibits good adhesion to those metal[20-22]. On the other hand, adhesion between polyimide and Cu is not good. Cu is diffused into polyimide layer as a carboxylate and makes weak adhesion layer[23-26]. In Fig. 7, left picture shows the Cu ion migration in polyimide by TEM. The dark spot is Cu ion.

Polyimide precursor structure has great influence on Cu migration. We find new polyimide precursor for positive tone photosensitive polyimide shows no Cu migration (Fig.7 right).

3.5 Chemical resistance and Tg improvement

Chemical resistance is much important for application of WL-CSP. Because polyimide should endure the wiring process, etching, flux treatment, and cleaning process. Especially, the flux treatment is the most severe in these processes,
because the treatment is carried out at 240-290°C.

In order to improve chemical resistance and Tg, cross-linked polyimides like bis-maleimide, ethynyl terminated polyimide[27], alcohoxy terminated polyimide[28], isocianate[29] were reported. Table 2 summarized our results. Most cross-linked materials were not effective. We think this reasons as follows. 1. Cross-linking reaction rate is small. 2. Flexibility of cross-linking material is higher than that of polyimide back bone.

We find an effective compound to improve the chemical resistance and Tg. By using this compound, we developed good chemical resistance positive PSPI "PW-1200" and "PW-1500". PW-1200 has excellent chemical resistance with good adhesion to various metals. PW-1500 is focused on low temperature curing. PW-1500 shows 253°C Tg at 250°C curing with good chemical resistance.

<table>
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<th>Table 2. Improvement of Tg and chemical resistance</th>
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<tr>
<td>Tg at 250°C curing</td>
</tr>
<tr>
<td>None</td>
</tr>
<tr>
<td>Bis maleimide</td>
</tr>
<tr>
<td>Ethynyl terminated</td>
</tr>
<tr>
<td>Bis epoxy</td>
</tr>
<tr>
<td>Triis isocianate</td>
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<tr>
<td>New compound</td>
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As shown below, good pattern shape for WL-CSP and fine pattern resolution with excellent adhesion to Si, Cu and molding compound as well as high Tg. Patterning condition and cross section of cured posi-PSPI patterns are shown in Fig.8.

Fig.8 Pattern condition and pattern profile of PW-1200

4. Conclusion

Adhesion between polyimide and molding compound is dominated by b-relaxation of polyimide. Lower b-relaxation polyimide shows higher adhesion.

We developed new excellent adhesion improving technique to Si substrate. Developed polyimide coatings which have excellent adhesion to Si wafers even after the HF treatment.

New developed polyimide which designed for positive tone photo sensitive polyimide coating exhibits no Cu migration nature.

We developed good adhesion promoter to Cu. The promoter compounds are useful to improve adhesion of positive-PSPI.

By investigating chemical resistance and Tg improving method, we developed effective method to improving those nature.

To adopt those techniques, we developed positive PSPI "PW-1200" and "PW-1500", those are suitable for bump protection and WL-CSP. The coating has excellent adhesion to molding compound, Cu as well as Si substrate, excellent chemical resistance and high Tg. PW-1200 shows excellent chemical resistance as well as high Tg with good adhesion to Si and Cu. PW-1500 focuses on low temperature curing nature. The coating is able to be cured at 250°C with 253°C Tg, good chemical resistance and good adhesion.

Reference

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