High-Modulus Negative Photosensitive Polyimide for i-line

Masahiko Yoshida, Tatsuya Hirata, Mitsuru Fujita, Nobuhiro Anzai, and Nobuchika Tamura

Fab Materials Research & Development Department, Electronics and Functional Products Division, Asahi Kasei E-materials Corporation, 2-1 Samejima, Fuji-shi, Shizuoka 416-8501, Japan

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1. Introduction

Polyimide (PI) is widely used in industry, because of its excellent heat resistance, chemical resistance, and high mechanical properties. In semiconductor field, photosensitive PI (PSPI) is used as passivation layer for chip surface protection, alpha particle shielding layer, stress buffer layer and interlayer dielectrics for re-distribution layer of semiconductor devices [1].

Semiconductor package design has been complicated due to the demand of high signal speed performance and packaging size miniaturization. Flip-chip packages with 40nm wafer node and beyond, ELK (extra low-k) / Cu interconnect is implemented. Fracture and / or delamination of ELK induced by thermal stresses have been observed due to their fragile nature and low mechanical strength [2].

PI layer would also be desired as a stress buffer function to protect fragile ELK layer. In our previous work, ELK protection factor of PI layer was investigated by finite element analysis. As a result, it was shown that modulus of PI has large effect to ELK protection, higher modulus contributes to release the concentrated stress at ELK layer [3].

On the other hand, g-line (436nm), h-line (405nm), i-line (365nm) are mainly used as exposure wavelengths for PSPI patterning, and i-line exposure is desired for fine pitch patterning in buffer coating process. Film transparency for i-line is a very important factor to complete photolithographic reaction from top surface to bottom of film. In general, i-line absorption of PSPI is in proportion to modulus, because rigid structure for high modulus increases imide concentration and / or intramolecular charge transfer transition. Therefore, patterning of PSPI which has high modulus for ELK protection by i-line is difficult because of high absorption. Thus, it is an important task to achieve both parameter “high modulus” and “low absorption”

Polymer absorption depends on the main structure and side chain of polymer, and modulus depends on the main structure. Therefore, we focus on side chain modification of polyimide precursor to achieve low absorption. This report describes novel negative-type photosensitive polyimide that has high modulus for ELK protection and has low i-line absorption for enough patterning performance by i-line.

2. Experimental

2.1. Synthesis of polyimide precursor

Synthesis of polyimide precursor is indicated in scheme 1. 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 16hr. N,N'-dicyclohexylcarbodiimide (DCC) was added to the solution with GBL under ice bath. Subsequently, diamine in GBL was added to the solution. The solution was stirred at room temperature for 2 hours. After the reaction, The
solution was filtered to remove \(N,N\)-dicyclohexylurea (DCU) as a by-product and poured into a large amount of water. The polymer precipitate was filtrated and dried under vacuum.

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

\[
\text{Y} \quad \text{N} \quad \text{R} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{Y} \quad \text{R} \quad \text{O} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{H} \\
\text{pyridine, DCC} \quad \text{GBL}
\]

Scheme 1. Synthesis of polyimide precursor. X and Y are aromatic structure. R is acryloyl group or non-acryloyl group.

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. Absorption measurement

Polymer was dissolved to NMP. Polymer solvent was coated on quartz glass and pre-baked. Absorbance of the coated film about 10 \(\mu\)m thick on quartz glass was measured by UV-Vis spectrometer (UV-1600PC, Shimazu).

2.4. 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.

2.5. Modulus measurement

The photosensitive polyimide precursor varnishes were filtered and coated on 6 inch silicon wafer and pre-baked (Tokyo Electron Mark-8). The coated film about 10 \(\mu\)m thick on a wafer was exposed through a patterning mask by i-line stepper (Nikon NSR2005i8A) from 100 mJ/cm\(^2\) to 800 mJ/cm\(^2\). The exposed film was developed with cyclopentanone and then rinsed with 2-propylene glycol-1-methyl ether acetate by a spray development (SOKUDO SC-W60A-AV9). The patterned film was observed by optical microscope.

2.7. Chemical resistance

The patterned film was cured at 300 \(^\circ\)C for 2 hours under N\(_2\) atmosphere. Resist stripper, organic solvents, metal etchants and flux were used as the test chemicals. The films were immersed in these chemicals under each condition. The tested films were rinsed by deionized water for 5 minutes and then dried at room temperature. Appearance after the test was observed by optical microscope. Thickness change after the test was measured by contact film thickness measuring apparatus.

3. Results and discussion

3.1. Modulus and absorbance of films using various polymers

As the negative-type PSPI, polyimide precursor with acryloyl groups in side chain is often prepared in terms of photosensitivity and varnish stability. Various polyimide precursors with only acryloyl groups in side chain were synthesized by applying various kinds of X and Y units till now. The result of absorbance at 365nm of the pre-baked film of various polyimide precursors, and modulus of cured film of polyimide precursors which have only acryloyl groups with side chain are shown in Fig. 1.

![Figure 1. The relationship between modulus of cured film and absorbance of pre-baked film at 365nm](image-url)
According to our experience, absorbance of pre-baked film of polyimide precursor at 365nm shall be less than 1.5 considering the photo crosslinking reaction from top to bottom by i-line. In our study, highest modulus of cured film of polyimide precursors with absorbance less than 1.5 are 4.0GPa. The modulus of polyimide or polybenzoxazole typically used as buffer coat is around 3.0GPa. Comparing with typical polyimide structure, modulus of photo-definable polyimide is not so high.

3.2. Effect of converting to non-acryloyl groups in side chain of polyimide precursor.

We focused the particular rigid main structure polyimide precursor, which has 5.2GPa modulus value and 1.68 absorbance value called “polymerA”. So the polyimide precursors which were converted from acryloyl groups into the particular non-acryloyl groups of polymerA were synthesized. The particular non-acryloyl groups represent some kinds of groups which have no ability of cross-link and low i-line absorption. The result of absorbance at 365nm of the polyimide precursors against conversion rate of non-acryloyl groups about polymerA is shown in Fig. 2.

![Figure 2. The relationship between absorbance at 365nm and conversion rate of side chain of polyimide precursors](image)

As the conversion rate from acryloyl groups to the non-acryloyl groups became higher, polymer absorption was decreased as shown in Fig. 2, and in case the conversion rate reached over 20%, absorbance was less than 1.5. The reason is supposed that the packing condition of pre-baked film between polymer to polymer of the polyimide precursor which is introduced the particular non-acryloyl groups become looser than that has only acryloyl groups in side chain, because the particular non-acryloyl group is bulky structure. The patterning result of polyimide composition by i-line is shown in Table 1. In case that the conversion rate is 0%, 10%, polyimide is delaminated from Si substrate. In case that the conversion rate is 90%, polyimide pattern is swelled and dissolved polyimide residue is remained on the opening area. However, in case that the conversion rate is 20-80%, the patterning condition is good as no delamination, no swelling, no residue and no distortion.

The suppositional reason of delamination when the conversion rate is 0% or 10%, is considered that the sufficient light does not reach to the bottom owing to high absorption of the film. On the other hand, when the conversion rate is 90%, the light reaches to bottom, but cross-linking reaction is insufficient due to lack of acryloyl groups of side chain. In case that the conversion rate is 20-80%, it is supposed that the light reaches to bottom, and acryloyl groups of side chain is sufficiently cross-linked.

<table>
<thead>
<tr>
<th>polyimide composition</th>
<th>conversion rate of side chain of polyimide precursor [%]</th>
<th>performance of patterning by i-line</th>
</tr>
</thead>
<tbody>
<tr>
<td>composition A</td>
<td>0</td>
<td>NG</td>
</tr>
<tr>
<td>composition B</td>
<td>10</td>
<td>NG</td>
</tr>
<tr>
<td>composition C</td>
<td>20</td>
<td>Good</td>
</tr>
<tr>
<td>composition D</td>
<td>30</td>
<td>Good</td>
</tr>
<tr>
<td>composition E</td>
<td>50</td>
<td>Good</td>
</tr>
<tr>
<td>composition F</td>
<td>70</td>
<td>Good</td>
</tr>
<tr>
<td>composition G</td>
<td>80</td>
<td>Good</td>
</tr>
<tr>
<td>composition H</td>
<td>90</td>
<td>NG</td>
</tr>
</tbody>
</table>

Polyimide precursor which is the particular rate of side chain converted from polymerA is called “polymerB”. The results of absorbance at 365nm of the pre-baked film and modulus of cured film of polymerA and polymerB were shown in Fig. 3. As is shown in Fig. 3, polymerB showed not only decrease of absorbance, but also increase of modulus. Such increase of modulus is considered that polyimide composition used polymerB is more interacted between molecules of polymer main structure than polymerA, because non-acryloyl groups are easier to volatilize than cross-linked acryloyl groups in polyimide composition film during cure. The modulus value of polymerB was 5.6GPa which is close to highest modulus of photosensitive polyimide.
3.3. Chemical resistance

Chemical resistance test of polyimide composition used polymerB was done for representative chemical as resist stripper, metal etchant and flux etc. Summary of chemical resistance test is shown in Table 2.

Table 2. Summary table of chemical resistance test

<table>
<thead>
<tr>
<th>Application</th>
<th>Chemical</th>
<th>Test condition</th>
<th>Film state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resist stripper</td>
<td>Organic amine / NMP / GBL / other</td>
<td>80deg.C 5min</td>
<td>Good</td>
</tr>
<tr>
<td>Organic solvent</td>
<td>Acetone</td>
<td>r.t. 15min</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>PGMEA</td>
<td>r.t. 15min</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>NMP</td>
<td>r.t. 15min</td>
<td>Good</td>
</tr>
<tr>
<td>Metal etchant</td>
<td>Nitric acid 30%</td>
<td>r.t. 10min</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid 30%</td>
<td>r.t. 10min</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>HF 1%</td>
<td>r.t. 5min</td>
<td>Good</td>
</tr>
<tr>
<td></td>
<td>Ti etchant</td>
<td>r.t. 5min</td>
<td>Good</td>
</tr>
<tr>
<td>Flux</td>
<td>Water soluble type</td>
<td>260deg.C reflow</td>
<td>Good</td>
</tr>
</tbody>
</table>

Usually, semiconductor package application such as Flip-Chip package uses re-distribution layer (RDL) and solder bump, and high chemical resistance is required for repassivation dielectric material. The package would be mounted on a circuit board during reflow process. NMP and / or GBL with organic amine chemical are used as dry film resist stripper for bump formation process. Metal etchant is used to form RDL and flux is used at reflow soldering process. These chemicals would be directly attached with polyimide surface in the bumping process. The result of chemical resistance test of polyimide composition used polymerB was shown no defect such as crack, thickness change, pattern distortion and discolor. In general, polyimides which have high transparency often show weak chemical resistance. There are two estimated reasons of weak chemical resistance. One reason is that the imide ring bond energy of high transparency structure is weaker than that of low transparency structure. Imide ring bond is cleaved by the strong alkali or acid, therefore, the imide ring bond energy is an important factor of chemical resistance. Second reason is that packing condition between polymer to polymer is sparse. In general, stacking condition of stiff main structure is dense because aromatic structures cause π–π stacking. However, polyimide composition used polymer shows high chemical resistance property even though the absorbance is low. It is supposed that the side chain unit is converted to make lower absorbance, and polymer stacking condition is densely kept. The side chain unit conversion is useful method to achieve high transparency, high modulus, and good chemical resistance.

4. Conclusion

The novel negative-type photosensitive polyimide precursor to protect ELK for Flip-chip package was developed. High modulus was achieved by the rigid structure of main polymer, and film transparency was achieved to modify the side chain unit by tuning the ratio of particular non-acryloyl groups and acryloyl groups. This polyimide composition showed high modulus value (nearly 6.0GPa) and could pattern by i-line. This polyimide composition also showed high chemical resistance property. Thus, this polyimide composition will be suitable for Flip-chip package to protect ELK as surface protective and interlayer dielectric film.

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References