Low Stress, High Modulus, Photosensitive Polyimide

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1. Introduction
Due to their excellent thermal, mechanical and electrical properties as well as good chemical resistance, polyimide (PI) and poly(benzoxazole) (PBO) have been widely used as stress buffer coatings and cover coating films for wafer level chip size packages that have copper re-routing distribution layers to improve the reliability of semiconductor devices [1, 2]. In addition, to simplify opening connection via or bonding windows, photosensitive PI (PSPI) and PBO (PSPBO) have become popular due to the elimination of photo-resist processes [3-5].

On the other hand, in order to shrink chip size and improve various performances of the chip, the design rule for the semiconductor chip is getting smaller. As a result, it is important to prevent wiring delay and, for this purpose, materials having low-dielectric constant are being applied as the insulating layer. Recent insulating layers use a pore structure to lower the dielectric constant but which results in the insulating layer being fragile. In order to protect this fragile insulating layer, high modulus and/or thicker film capability are required for the material to be used as a protection layer [6-7]. In addition, as the chip and the wafer are getting thinner, it is necessary to avoid warpage and, for this purpose, low stress is required. The stress is calculated by the following equation (1) [8].

\[ \sigma = K (\alpha_p - \alpha_s) (T_p - T) E_p \]  

\( \sigma \): wafer stress, \( \alpha_p \): CTE for polyimide, \( \alpha_s \): CTE for silicon wafer, \( T_p \): glass transition temperature of polyimide, \( T \): measuring temperature, \( E_p \): Young's modulus of polyimide, \( K \): constant

Equation (1) indicates that lower modulus, lower glass transition temperature and lower CTE reduce stress. On the other hand, thicker film thickness results in higher stress. So, low stress requirement contradicts high modulus and thicker film capability.

Furthermore, low temperature curability is also required for the material to improve chip yield. In order to meet these requirements, a negative-tone, low stress, high modulus material based on polyimide technology was developed that can be cured below 300°C.

2. Experimental
2.1. Materials
Monomers, additives and solvents were used as purchased. HD-4104 is a standard PI material produced by Hitachi Chemical DuPont MicroSystems Ltd. and was used as a reference.

2.2. Synthesis of polyamic acid ester
The polyamic acid ester used in this study was synthesized by the reaction of acid chloride intermediate and diamine shown in Figure 1.

2.3. Evaluation of a model composition
A photosensitive polyamic acid ester varnish was prepared by adding the polymer, a photo-initiator, a cross-linkable monomer, adhesion promoters and the other additives to
The varnish was filtered with 3μm filter before being spin-coated onto silicon wafers and then prebaked on a hot plate at 120 °C for 3 minutes. The prebaked wafers were exposed to i-line radiation using an i-line stepper and developed with cyclopentanone using the puddle method. The patterned wafers were finally cured at 270 °C, 300 °C and 350 °C under nitrogen respectively.

2.4. Thermal and mechanical properties

The varnish was coated, soft-baked and blanket exposed onto 6 inch silicon wafers and then cured at 270 °C for 4 hours, 300 °C for 1 hour and 375 °C for 1 hour under nitrogen flow. The residual stress of the samples was measured by a thin film stress measurement system. Tensile strength, elongation and Young’s modulus were measured on 10μm thickness films after cure with a tensile tester. The glass transition temperature (Tg) and the coefficient of thermal expansion (CTE) were measured by a thermo-mechanical analyzer.

2.5. Evaluation of chemical resistance to Dynastrip-7700 and NMP.

The patterned films were cured at 270 °C for 4 hours, 300 °C for 1 hour and 375 °C for 1 hour under nitrogen flow. The cured films were dipped in Dynastrip-7700 or NMP at 70 °C for 30 min, rinsed with deionized water for 5 minutes and then dried at room temperature before drying the film at 150 °C for an additional 16 hours. Film thickness measurements using a surface profiler and an appearance check of the films using an optical microscope were conducted both before and after the final drying of the films respectively.

3. Results and discussion

3.1. Scouting of polyamic acid ester

In order to obtain a high modulus PI, it is necessary to apply a rigid structure to the polymer back-bone. In addition, proper i-line transparency is required with the polyamic acid ester which is the precursor of the PI for the photosensitive material. Finally various cross-linkable monomer combinations were also evaluated and the composition of polymer set.

3.2 Lithographic property

The lithographic property was evaluated for a 10μm cured film thickness and fine patterns obtained with 250 mJ/cm² i-line exposure after development. The thicknesses after prebaking and development were 17μm and 16.2μm respectively. As shown in Figure 2, good resolution could be seen from the cross-sectional image by SEM observation.

3.3 Mechanical and thermal properties

Mechanical and thermal properties of the developed material with different cure temperatures together with HD-4104 are shown in Table 1. The developed material shows high modulus (> 6GPa) and low stress (< 20MPa) in the cure temperature range from 300°C to 350°C when compared with our standard PI, HD-4104.

3.4 Chemical resistance

One of the important requirements for the protection layer is chemical resistance, because the cured film is exposed to various chemicals during the bump making processes. As typical chemicals include dry film strippers and resist strippers, chemical resistance tests were conducted using Dynastrip 7700 (dry film stripper) and NMP (main component of resist stripper).
The chemical resistance of the initial setting material (Run1) was not good even when cured at 350°C. Dissolution of the film or swelling was observed after treatment with both Dynastrip 7700 and NMP, respectively. It is considered that the chemical resistance performance of the cured film at 350°C to these chemicals is essential property for the polymer backbone, because slight components from the cross-linker remain in the cured film at 350°C.

In order to improve chemical resistance against Dynastrip and NMP, various compositions were evaluated by changing the cross-linkable monomer to focus on the backbone, linkage and the number of cross-linkable group. The image of the cross-linker is shown in Figure 3.

As can be seen in Table 2, chemical resistance was greatly affected by the cross-linker’s backbone, linkage and number of cross-linkable group when the film was cured at below 300°C.

Finally, we set the material having good chemical resistance without sacrificing the original thermal and mechanical properties by selecting a suitable cross-linkable monomer.

### 4. Conclusion

We developed a solvent developable, negative-tone, low stress, high modulus PI that can be cured below 300°C. The chemical resistance of the initial setting material in Dynastrip 7700 and NMP was not good but subsequently improved by selecting a suitable cross-linkable monomer without significantly sacrificing original thermal and mechanical properties.

### References

3. R. Rubner, H. Ahne, E. Kuhn, and G. Kolo-

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**Table 1 Cured film properties**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Cure temp. (ºC)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>Elongation (%)</th>
<th>Tg (ºC)</th>
<th>CTE (ppm/K)</th>
<th>Residual stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HD-4104</td>
<td>375(1hr)</td>
<td>200</td>
<td>3.5</td>
<td>45</td>
<td>325</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>350(1hr)</td>
<td>220</td>
<td>6.5</td>
<td>20</td>
<td>324</td>
<td>22</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>300(1hr)</td>
<td>325</td>
<td>6.1</td>
<td>48</td>
<td>298</td>
<td>40</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>270(4hr)</td>
<td>290</td>
<td>4.9</td>
<td>50</td>
<td>297</td>
<td>28</td>
<td>20</td>
</tr>
</tbody>
</table>

**Table 2 Results of chemical resistance tests**

<table>
<thead>
<tr>
<th>Run</th>
<th>Cross-linkers</th>
<th>Chemical resistance test results at different cure temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Backbone</td>
<td>Dynastrip 7700 NMP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270ºC/4hr 300ºC/1hr 350ºC/1hr 270ºC/4hr 300ºC/1hr 350ºC/1hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dissolving Dissolving Acceptable Dissolving Acceptable Dissolving Good</td>
</tr>
<tr>
<td>1</td>
<td>Polyethylene glycol Ester 2</td>
<td>Good</td>
</tr>
<tr>
<td>2</td>
<td>Pentaerythritol Ester 4</td>
<td>Good</td>
</tr>
<tr>
<td>3</td>
<td>Pentaerythritol Ester 6</td>
<td>Good</td>
</tr>
<tr>
<td>4</td>
<td>Cyanuric acid Urethane 6</td>
<td>Good</td>
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