Photoneece Low Temperature Curing Series

Toray Industries
About Toray  Photoneece ■

■Photoneece ■is photosensitive polyimide coatings which developed Toray by awarded* original technologies. Currently, the ■Photoneece ■are widely used as a buffer coating for semiconductor devices, micro-lens for image sensors, insulator for OLED, interlayer-dielectrics for electronic components and so on.

Toray ■Photoneece ■is world leading photosensitive polyimide coatings for semiconductor, display and electronic devices.

To maintain our current status, we are developing low residual stress type photosensitive polyimide coatings.

*: Technical award from Chemical Society Japan (2009) by development of positive tone photosensitive polyimide by partial esterification of polyimide precursor.
  Technical award from Polymer Society Japan (1991) by development of ionic bonded type negative tone photosensitive polyimide.
Polyimide coatings for next generation

**High speed connection** → **Bump connection (WL-CSP)**

- **Stress Concentration**
  - Solder
    - CTE: 20 ppm/℃
  - LSI chip
    - CTE: 4 ppm/℃
  - Polyimide
    - CTE: 40 ppm/℃
  - Underfill
    - CTE: 70-150 ppm/℃
  - Board
    - CTE: 20 ppm/℃

**Smaller feature of LSI** → **Device structure, materials change**

- **Low stress (Thick coat)**
  - Low thermal curing thick coatings

- **Lower thermal budget**

- **High K gate insulator**
  - Weak for heat treatment

- **Porous Low K + Cu wiring**
  - Mechanically weak

Toray proprietary
Low temperature cure for next generation buffer coating

Cure temp. <200°C (Low thermal budget), Heat stability >300°C (Solder process)

Low temp. curable PSPI

Polyimide (High temp. cure)

Imidization conversion (>300°C)

Soluble PI
- No imidization
- New cross-linker working at 150°C

Epoxy Acrylic

Low temp. curable PSPI

New cross-linker working at 150°C

Polyimide (High temp. cure)

Low temp.

Process temperature (°C)

Degradation temperature [°C]

0 100 200 300 400

Low temp.

High temp. (Solder process)
Low cure temperature polyimide design

<Requirements>
1. Less damage to device during PI cur---Less thermal budget
2. Applicable to super thin chip---Less stress to wafer
3. More protective film----------Thicker film applicable(20-30um)

<Design concept>

Key concept for New polyimide: Low molecular weight polyimide change into polyimide molecular weight by heat treatment. High molecular weight polyimide contribute to realize tough film after post cure

Polyimide  \(\xrightarrow{150\sim 180\text{C}}\)  Macromolecule of Polyimide
### Features of PN-Series

1. **Negative tone and Alkali Developable (2.38% TMAH)**

2. **Low Shrinkage after Cure: about 10% (Good Planarization, Low Stress)**

3. **Wide Cure temperature Range (165-300 °C)**

4. **Good Mechanical Properties as well as conventional Polyimides**

5. **Sufficient Chemical Resistance to Bumping Processes**

6. **Good Thermal Stability >300 °C (~200 °C)**
Patterning Process of PN-2000(1500cp)

<table>
<thead>
<tr>
<th>Process</th>
<th>1500cP Details</th>
<th>1500cP Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spincoat</td>
<td>700rpm for 10sec and 1500rpm for 30sec</td>
<td>700rpm for 10sec and 2300rpm for 30sec</td>
</tr>
<tr>
<td>Prebaking</td>
<td>100°C × 3min (Hot plate) (Thickness: 18.1 μm)</td>
<td>100°C × 3min (Hot plate) (Thickness: 12.3 μm)</td>
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<tr>
<td>Exposure</td>
<td>400mJ/cm² (800msec) (g, h, i-line)</td>
<td>300mJ/cm² (600msec) (g, h, i-line)</td>
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<tr>
<td>PEB</td>
<td>100°C × 1min (Hot plate)</td>
<td>100°C × 1min (Hot plate)</td>
</tr>
<tr>
<td>Development</td>
<td>40s × 2 Puddle development (Thickness: 17.4 μm) *2.38% TMAH solution</td>
<td>30s × 2 Puddle development (Thickness: 11.7 μm) *2.38% TMAH solution</td>
</tr>
<tr>
<td>Curing</td>
<td>200°C for 60min (N₂) (Thickness: 15.0 μm)</td>
<td>200°C for 60min (N₂) (Thickness: 10.0 μm)</td>
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</tbody>
</table>
Negative Tone Type

**Patterning profile of PN-2010**

PB $100 \times 3$min Exposure dose $250$ mL/cm² PEB $100 \times 1$min Development $30$ s $^2$

<table>
<thead>
<tr>
<th>F</th>
<th>4umL&amp;S</th>
<th>F</th>
<th>5umL&amp;S</th>
<th>F</th>
<th>10umL&amp;S</th>
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Toray proprietary
<table>
<thead>
<tr>
<th>Negative Tone Type</th>
<th>Curing condition ℃</th>
<th>350X1h</th>
<th>280X2h</th>
<th>200X1h</th>
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<tr>
<td>Tensile strength MPa</td>
<td>122</td>
<td>119</td>
<td>108</td>
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<tr>
<td>Elongation %</td>
<td>25</td>
<td>40</td>
<td>34</td>
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<td>Young's Modulus Gpa</td>
<td>3.9</td>
<td>3.3</td>
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<td>Residual stress MPa</td>
<td>48</td>
<td>41</td>
<td>36</td>
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<td>5% weight loss temp. ℃</td>
<td>434</td>
<td>401</td>
<td>382</td>
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<td>Tg(TMA) ℃</td>
<td>334</td>
<td>284</td>
<td>201</td>
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<td>Dielectric constant 1MHz</td>
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<td>Volume resistance Ω・cm²</td>
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<td>Surface resistance Ω・cm</td>
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<td>Water absorption %</td>
<td>1.4</td>
<td>1.4</td>
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Developer PN-2000 2.38% TMAH
Features of Positive Low Temp. "Photoneece"

- Low Temperature Curable (~200 ℃) (Less Damage to Devices)
- Low Shrinkage after Cure: about 10% (Good Planarization, Low Stress)
- Common 2.38% TMAH Developable
- Good Mechanical Properties as well as conventional Polyimides
- Sufficient Chemical Resistance to Bumping Processes
- Good Thermal Stability >300 ℃
- Fine Patterning Properties
We successfully developed “Positive tone Photo Definable Polyimide Coatings” by combining our long history of polyimide designing technologies and our competitive photo sensitive polymer technologies.
## Conditions

- **Prebaking**: 120 °C, 180 sec
- **Exposure**: 5000 J/m² at i-line (Eth= 3500 J/m²)
- **Development**: 40 sec by 2.38% TMAH
- **Cure**: 200 °C, 1 h

### Prebaked film thickness = 6.2um
- **Thickness after Development**: 5.6um
- **Thickness after Cure**: 5.1um, **Shrinkage**: 9%

<table>
<thead>
<tr>
<th></th>
<th>3 um</th>
<th>5um</th>
<th>10um</th>
<th>20um</th>
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Toray Polyimide Coatings Line-up

Polyimide Coatings

- Non Photo
- Semicofine
- Negative
- Positive
- Photoneece

- Patterning by Photo-resist, Many steps
- Less Resolution (< 30 μm)
- Organic solvent develop, Expensive
- Resolution limit is about 10 μm

- < Insoluble by exposure >
- Alkali developable
- Resolution limit is about 3 μm

- < Soluble by exposure >

- PW-1200, PW-1500
- PW-2000 series
- PW-1900
- PW-3000 series

- Buffer Coat
- Lead Frame

- Stress Buffer Coat
- Thermal, Electrical, Mechanical properties
- EMC

- Positive Low Temp.
- Photoneece PN-series

- Adhesion to Au

- SP-042: CTE 18ppm
- BG-2430: CTE 25ppm
- SP-341: Elongation 100%
- BG-8440: Insoluble

- Toray proprietary