Development of Photosensitive Polyimides for LCD with High Aperture Ratio

May 24, 2004

LG Chem
Outline

• Why is polymer dielectric required for TFT LCD?
• Requirements of the polymer dielectrics
• What is polyimide?
• Problems of the polyimides
• Development of colorless photosensitive polyimide
• Application
Why is Polymer Dielectric Required for TFT LCD?

TRANSMISSION OF LCD COMPONENTS

<table>
<thead>
<tr>
<th>Item</th>
<th>Transmittivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass substrate</td>
<td>95</td>
</tr>
<tr>
<td>Aperture ratio</td>
<td>40~60</td>
</tr>
<tr>
<td>Polarizer</td>
<td>35~36</td>
</tr>
<tr>
<td>Color filter</td>
<td>25</td>
</tr>
<tr>
<td>Total</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Development New LCD Devices

(a) Passivation layer

Black matrix

LC

ITO glass

Column line

(b) Passivation layer

with low dielectric constant

Black matrix
# Dielectric Materials for TFT LCD

<table>
<thead>
<tr>
<th>Property</th>
<th>Inorganic material</th>
<th>Polymeric material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric constant</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Processability</td>
<td>CVD</td>
<td>Spin coating</td>
</tr>
<tr>
<td>Flexibility</td>
<td>rigid</td>
<td>flexible</td>
</tr>
</tbody>
</table>
Typical Polymer Dielectrics (I): BCB of Dow Chem.

B-staging → Oligomer

FW = 375

- Transmittance: No conjugation beyond styrene, No heteroatom except O & Si
- Excellent Planarization by Low MW design
- Still have Processability: Not crystalline due to Si-O-Si linkage
- Reactive End-functionality: easily crosslinkable by cyclobutene group
- Heat Resistance: No thermal degradation component
- Solubility Limitation: Nonpolar aromatic solvent
- Curing in the absence of Oxygen required
- Extra Adhesion Promotor required
Typical Polymer Dielectrics (II): Photoacryl of JSR

- Transmittance: Acryl based material
- Alkaline Solution Developable
- Process window: Easy formulation control
- Heat Resistance: Acrylic component
- Relatively low Price

Photo polymerization
## Comparison of Organic Dielectrics

<table>
<thead>
<tr>
<th>Type</th>
<th>Photo-Acryl</th>
<th>BCB (Dry-Etch)</th>
<th>PSPI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maker</strong></td>
<td>JSR, etc</td>
<td>DOW</td>
<td>LGC/KRICT</td>
</tr>
<tr>
<td><strong>Status</strong></td>
<td>commercialized</td>
<td>commercialized</td>
<td>developing</td>
</tr>
<tr>
<td><strong>Patterning</strong></td>
<td>OK</td>
<td>No*</td>
<td>OK</td>
</tr>
<tr>
<td><strong>Dielectric Constant</strong></td>
<td>3.4</td>
<td>2.65</td>
<td>3.5 (expected)</td>
</tr>
<tr>
<td><strong>Heat Resistance</strong></td>
<td>250°C</td>
<td>&gt; 300°C</td>
<td>300°C</td>
</tr>
<tr>
<td><strong>Transmittance at 400nm</strong></td>
<td>93%</td>
<td>97%</td>
<td>93%</td>
</tr>
<tr>
<td><strong>Planarization</strong></td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
<tr>
<td><strong>Water absorption</strong></td>
<td>high</td>
<td>low</td>
<td>High</td>
</tr>
<tr>
<td><strong>Curing</strong></td>
<td>air</td>
<td>N₂ atmosphere</td>
<td>air</td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>&lt; 10µm</td>
<td>-</td>
<td>15µm</td>
</tr>
<tr>
<td><strong>Price</strong></td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
</tbody>
</table>

* Solvent Develop Type
**Dry-Etch BCB : Problems in processing condition and price
Requirement of Polymer Dielectrics

- Chemical resistance and heat resistance
- Photo-sensitivity
- Adhesion
- Transmittance
- Planarization
- Low dielectric constant

Diagram elements:
- Gate bus line
- Data bus line
- Liquid crystal
Why is Polyimide Required for TFT LCD?

Crystalline   Amorphous

Commodity Plastics

Engineering Plastics

Super Engineering Plastics

Price

Heat resistance

PI

PEEK LCP PPS

PAI PEI PES

PAR

PC m-PPO

PE

PP

ABS PS PMMA

High

PA POM PBT PET

High
What is Polyimide?

• Structure

• Synthesis

[Diagram of polyimide structure and synthesis process]

Insoluble and Infusible
Characteristics of Polyimide

- Excellent Thermal and Cyrogenic Temperature Stability: 
  -269~400°C

- Wear and friction properties

- Radiation and Oxidative Stability
  Excellent Electrical and Mechanical Properties (TS : 1,700 kg/cm²)

- Inherently Flame Retardancy (LOI : 37, UL 94 V-0)

- Good Chemical Resistance
Weak Point and Solutions of Polyimide (I)

(I) Transmittance

Polyimides may stack like this allowing the carbonyls of the acceptor on one chain to interact with the nitrogens of the donor on adjacent chains.

Nitrogen atoms have a higher electron density than the carbonyl groups and lend it to the acceptor.

Carbonyl groups suck electron density away from the acceptor unit.
(II) Photosensitivity

Why is photosensitive dielectric layer required?
## Advantage of photosensitive polyimide

<table>
<thead>
<tr>
<th>Step</th>
<th>Traditional Process</th>
<th>New Process using PSPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Coupler</td>
<td>Coating</td>
<td>Coating</td>
</tr>
<tr>
<td>2. PI precursor</td>
<td>Thermal treatment</td>
<td>UV irradiation</td>
</tr>
<tr>
<td>3. PR</td>
<td>Coating</td>
<td>Developing</td>
</tr>
<tr>
<td>4. PI pattern</td>
<td>Drying</td>
<td>Removal of coupler</td>
</tr>
<tr>
<td></td>
<td>UV irradiation</td>
<td>Washing/drying</td>
</tr>
<tr>
<td></td>
<td>Developing</td>
<td>Removal of Drying</td>
</tr>
</tbody>
</table>

**Conventional patterning process**  **New process using PSPI**
Weak Point and Solutions of Polyimide (III)

(III) Degree of planarization

Topography- induced LC disclination at pixel edges  ➔ Low contrast ratio

Diagram showing a structure with layers labeled as ITO glass, Polymer dielectric, and Glass substrate.
Development of Novel Alkali-Developable Photosensitive Polyamic Acid (PAA)
Molecular Design of Photosensitive Polyamic Acid

- TFT, ITO deposition
- Processability
- High Aperture ratio
- Pattern formation
- Hest resistance
- Chemical resistance
- Transmittance, Dielectric constant
- Photo-patternability
- Aromatic group
- Crosslinking group
- Alicyclic group
- Photosensitive group

Adhesion

Degree of planarization

Polyimide precursor (PAA)

Photosensitive low dielectric materials
**Positive vs. Negative Type PSPI**

**Advantage of Positive PSLD**
- Lower defect image from dust or crack on mask
- Suitable for hole formation
- Better processability
- Base Developable (No Swelling: Higher resolution)
- High Photo-sensitivity (Chemical amplification)
- High aspect ratio

**Advantage of Negative PSLD**
- Low shrinkage
- No by-product
- Colorless
- Base Developable (No Swelling)
Chemistry of Negative Type PSPI

1. Mask
2. PSPI precursor
3. Substrate
4. UV

Prebake → UV exposure → Post exposure bake

Precursor polymer (PAA)

Formation of Crosslinked structure

Removal of Non-Exposed Area

Pattern Formation
### Synthetic Results of the PAAs with various MW

<table>
<thead>
<tr>
<th>Polyamic acids&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Molar ratio of monomers&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Molecular weight (g/mol)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>M&lt;sub&gt;W&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</th>
<th>MWD&lt;sup&gt;f&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA-1</td>
<td>3 : 2 : 2</td>
<td>17,900</td>
<td>14,600</td>
<td>1.23</td>
<td></td>
</tr>
<tr>
<td>PAA-2</td>
<td>10 : 9 : 2</td>
<td>43,600</td>
<td>27,100</td>
<td>1.61</td>
<td></td>
</tr>
<tr>
<td>PAA-3</td>
<td>15 : 14 : 2</td>
<td>49,900</td>
<td>31,800</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>PAA-4</td>
<td>1 : 1 : 0</td>
<td>101,200</td>
<td>81,600</td>
<td>1.24</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Polyamic acids

<sup>b</sup> Molar ratio of monomers (A:B:C)

<sup>c</sup> Molecular weight (g/mol)

<sup>d</sup> M<sub>W</sub>

<sup>e</sup> M<sub>n</sub>

<sup>f</sup> MWD
Thermal Properties of the PAAs

![Graph showing the thermal properties of PAAs](image)
Effect of MW of PAAs on Transmittance at 400 nm

[Graph showing transmittance (%) against wavelength (nm) for PAA-1, PAA-2, PAA-3, and PAA-4.]
## Chemical Resistance of PAAs

<table>
<thead>
<tr>
<th></th>
<th>NMP</th>
<th>DMAc</th>
<th>2.38 wt% aq. TMAH</th>
<th>PR stripper</th>
<th>MeOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA-1</td>
<td>99</td>
<td>99</td>
<td>100</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>PAA-4</td>
<td>98</td>
<td>99</td>
<td>100</td>
<td>100</td>
<td>99</td>
</tr>
<tr>
<td>PAE-1</td>
<td>100</td>
<td>99</td>
<td>100</td>
<td>96</td>
<td>99</td>
</tr>
</tbody>
</table>
# Chemical Resistance for PR Stripper of PAA-1

<table>
<thead>
<tr>
<th>Processing condition</th>
<th>Solubility for PR stripper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80°C, 7min</td>
</tr>
<tr>
<td>250°C, for 30 min</td>
<td>Insol</td>
</tr>
<tr>
<td>250°C for 1hr</td>
<td>Insol</td>
</tr>
<tr>
<td>250°C for 2hr</td>
<td>Insol</td>
</tr>
</tbody>
</table>
Effect of MW on Degree of Planarization

Degree of Planarization = \((1 - \frac{t_1}{t_2}) \times 100\)

Measured by \(\alpha\)-step 500

Pattern width (\(\mu m\))

Degree of Planarization (%)

Pattern width (\(\mu m\))

MW
DOP

DOP
Pattern width

Mi Hie Yi / KRICT
**Photolithography Process of PAAs**

1. **PSPI precursor**
   - **Mask**
   - **Substrate**
   - **UV**

2. **Prebake**
   - **90°C, 2 min**

3. **UV exposure**
   - **Exposure dose:**
     - **200 mJ**

4. **Post exposure bake**
   - **160°C, 10 min**

5. **Development**
   - **2.38% aq. TMAH**

6. **Curing**
   - **250°C, 60 min**

**Polyimide precursor**
- **Crosslinked polyamic acid**
- **Partially Imidized polyimide**
- **Development process**
- **Crosslinked polyimide**
Effect of an Exposure Dose on a Normalized Film Thickness of PAA-1

![Graph showing the effect of exposure dose on normalized film thickness. The x-axis represents exposure dose (mJ/cm²) ranging from 100 to 400, and the y-axis represents normalized film thickness (d₁/d₀) ranging from 0.0 to 1.2. Two curves are shown: one for CGI-124 (black) and another for Igacure-651 (red). The graph illustrates how the normalized film thickness increases with exposure dose for both materials.]
Effect of an Amount of Photoinitiator on a Normalized Film Thickness of PAA-1

![Graph showing the effect of photoinitiator amount on normalized film thickness.](image)
Typical Negative Patterns of PAA-1
(Film thickness : 2\(\square\))

Line width : 25\(\square\)

Line width : 20\(\square\)

Line width : 8\(\square\)

Line width : 8\(\square\)

Mi Hie Yi / KRICT
Typical Negative Patterns of PAA-1
(Film thickness : 35㎛)
Development of High Aperture LCD

(a) Black matrix
Passivation layer: SiNx

(b) Black matrix
Organic Passivation layer

LC
ITO glass
Column line
s

d
ε
Typical Application of Polymer Dielectrics (II)

TOC Technology

Conventional structure

- Aperture Ratio ~ 65%
- Assembly Margin ~ 5µ
- Total Pitch Problem

TOC structure

- Aperture Ratio ~ 72%
- Assembly Margin ~ 1µ
- Free from Total Pitch Problem

Overcoat for TOC