Novel Photosensitive Transparent Heat Stable Coatings

Mitsuhito Suwa, Takenori Fujiwara, Toru Okazawa, and Hitoshi Araki

Electronic and Imaging Materials Research Laboratories, Toray Industries, Inc.
1-2, Sonoyama 3-chome, Otsu, Shiga 520-0842 JAPAN
Mitsuhito_Suwa@nts.toray.co.jp

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1. Introduction
Optical devices are applied such as mobile telephone, digital camera, PC, touch sensor panel and so on. Many colorless and transparent organic materials, that are acrylic, novolac, and polyimide materials, are used as planarization layer for thin film transistor in liquid crystal device and outer micro lens on CCD and CMOS image sensors and so on [1]. However, the device manufacturing window was narrow, due to those maximum heat resistance temperature is about 230°C, view point of coloration and decomposition. As the result, it would be difficult for device maker to show good performance without any process change.

Recently we developed novel photosensitive transparent heat stable coatings [2-3]. They show fine patterning properties, no coloration, excellent transparency and good heat stability. The coatings are ideal for optical devices due to them.

In this paper, we introduce the novel materials from the point of photolithographic performance and film properties

2. Method
2.1 Materials
We used two coatings of “Photoclear” SP-series (SP-P5100 and SP-P8000) as novel photosensitive transparent heat stable coatings. The heat stable polymers of polysiloxane base synthesized by TORAY’s laboratory were used in the coatings. All compounds without the heat stable polymers and solvent were purchased and provide from chemical manufactures and used for experiments without further purification.

2.2 Patterning process and evaluation
The SP-series solutions were coated by spin coater (Mark-7, Tokyo Electron Limited) on a 6 inch glass wafer to obtain 2 micro-meter thickness after 230°C curing.

The coated wafers was baked at hot plate (100°C for 120sec, Mark-7)

The baked glass wafer was exposed by a broad band aligner (PLA-501F, Canon Inc.) with 300mj/cm² (at 365nm) through a gray-scale mask.

The exposed wafer was developed by 2.38% tetramethylammonium hydroxide aqueous solution (TMAH) using Mark-7. Developed patterns of SP-series were observed by optical microscopy.

After the development, film thicknesses of different exposed area were measured by STM-802 (Dainippon Screen Mfg. Co., Ltd.).

Half of developed wafers were treated by broad band exposure by PLA-501 with 300mj/cm² at 365nm. The exposure treatment was called as “bleaching”.

The exposed and unexposed wafers were treated at 230°C and 420°C for 60 min by using INH-21CD (Koyo Thermo Systems Co., Ltd) individually.

After the heat treatment (curing), every film thicknesses were measured by STM-802 (produced by Dainippon Screen Mfg. Co., Ltd.).

Scanning Electron Microscopy (SEM)
SEM measurement of the cured film of SP-P5100 to glass substrate was carried out after curing after bleaching and without bleaching wafer to obtain cross-sectional view of lithographic pattern (see Figure 1).
Photosensitivity evaluation

Developed film thickness dependency of SP-P5100 on exposure dose was summarized at figure 2.

Transparency evaluation

Wavelength dependency on transparency of the cured SP-P5100 and SP-P800 films was evaluated at a range from 300nm to 800nm by using MultiSpec-1500 (Shimadzu Corporation). Figure 3 and table 1 show the test results on glass substrate.

Chemical resistance evaluation

Chemical resistance of the cured SP-P5100 film of three substrates was tested by immersion in chemicals under various conditions. Table 2 shows the test result of glass, ITO, and Cr substrates.

Adhesion evaluation

Adhesion of the cured SP-P5100 film to various substrates was determined by a Scotch tape® delamination method (JIS K 5400) after PCT treatment. PCT (pressure cooker test) means a kind of accelerated test whose condition is 121°C, 2.0x10^5Pa (2.0atm), and 100%RH. Table 3 summarizes the test result of glass, ITO, SiO₂, and Cr substrates.

Heat stable evaluation

Thermo gravimetric apparatus TGA-50 (Shimadzu Corporation) was used to measure a weight change at a heating rate of 10°C/min up to 500°C in nitrogen atmosphere. 1% and 5% weight loss at temperature of SP-P5100 and SP-P8000 were determined. Figure 4 and table 4 show the test results.

3. Results

3.1 Scanning Electron Microscopy (SEM)

We obtained a good positive tone lithography pattern by ordinary photo lithographic process. As shown in figure 1, the SP-P5100 shows good round pattern profile and fine resolution after curing regardless of bleaching or not.

3.2 Photosensitivity

As shown in figure 2, the SP-P5100 shows the photospeed of 18mJ/cm². It shows higher sensitivity than usual transparent coatings composed of acrylic polymers.

3.3 Transparency evaluation

Color change after heat treatment is important for applying the material as optical devices. A ratio of the coloration was estimated by investigating transparent change at 400nm. As shown in Figure 3 and Table 1, the SP-P5100 showed good transparency in wavelength range of 400-800nm and small transparent change after 230°C curing regardless of having bleaching or not (99.1% ~ 96.5%). The SP-P8000 showed good transparency in wavelength range of 400-800nm and 95.5% per 2µm at 400nm after 420°C curing. The cured SP-P8000 exhibits excellent heat stability.

3.4 Chemical resistance evaluation

Table 2 shows chemical resistance of SP-P5100, SP-P8000 which does not any change by immersion in various chemicals on glass, ITO and Cr substrates. These results represent SP-5100 and
SP-P8000 have good chemical resistance.

Table 2. Chemical resistance of SP-P5100 and SP-P8000.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Condition</th>
<th>Substrate</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMAH (2.38 wt%)</td>
<td>23°C/180s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td>Resist stripper A MEA/BDG =15:85 (wt ratio)</td>
<td>45°C/180s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ITO</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>no change</td>
</tr>
<tr>
<td>TOK-106 MEA/DMSO ~70/30 (wt ratio)</td>
<td>60°C/180s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ITO</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>no change</td>
</tr>
<tr>
<td>Oxalic acid (3.5 wt%)</td>
<td>35°C/180s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ITO</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>no change</td>
</tr>
<tr>
<td>ITO etcher A HCl/KCl/H2O =6/8/84 (wt ratio)</td>
<td>35°C/180s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ITO</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>no change</td>
</tr>
<tr>
<td>Metal etcher HNO3/CH3COOH/H3PO4/H2O (5/5/80/10) (wt ratio)</td>
<td>40°C/150s</td>
<td>Glass</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ITO</td>
<td>no change</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr</td>
<td>no change</td>
</tr>
</tbody>
</table>

SP-P5100 have good chemical resistance.

3.5 Adhesion evaluation

Table 3 shows adhesion of SP-P5100 which does not delaminate on various substrates under PCT treatment. These results indicate splendid adhesion of AP*P5100 on them.

Table 3. Adhesion of SP-P5100 to various substrates after curing.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>PCT* treatment time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Glass</td>
<td>0/10**</td>
</tr>
<tr>
<td>ITO</td>
<td>0/10</td>
</tr>
<tr>
<td>SiO2</td>
<td>0/10</td>
</tr>
<tr>
<td>Cr</td>
<td>0/10</td>
</tr>
</tbody>
</table>

*PCT condition: 121°C, 2.0x10^6Pa (2.0atm), and 100%RH
**Delamination ratio; the number of delaminated parts/the number of all test parts. “0/10” means no delamination.

3.6 Heat stable evaluation

1% and 5% weight loss at the temperatures are important index to evaluate heat stability. Figure 4 and Table 4 show the thermal stability of SP-P5100 after curing at 230°C. It shows higher weight loss at the temperature (1wt%: 377d°C, 5wt%: 475°C) than usual transparent coatings composed of acrylic polymers (1wt%: 275 °C 1 , 5wt%: 322 °C ). Consequently, cured SP-P5100 showed excellent heat stability.

4. Conclusion

We developed the novel photosensitive transparent heat stable coatings “Photoclear” SP-series. The coatings had good photolithographic performance, chemical resistance, and adhesion. In addition to these properties, SP-series had excellent transparency and heat stability. These features will promise that SP-series are suitable for the optical device application.

References