PHOTOSENSITIVE POLYIMIDE/SILICA HYBRIDS

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Polyimide (PI) is a type of high performance polymer material characterized by its distinguished thermal stability. It also possesses excellent mechanical and electrical properties and has been widely applied in aerospace, electrical and microelectronic industries. In a traditional microelectronic application, PI is used as the insulating layer while a photoresist is used as a mask to provide the photolithographic pattern. This type of technology results in a complex processing procedure and also an unfavorable resolution caused by the wet development process. Therefore, PI precursors or soluble PIs that are photosensitive (photosensitive PI) provide a much simplified and safer processing steps.

The introduction of well dispersed (in nanometer size favorably) inorganic particles to the polymer matrix has been found to be extremely effective in the improvement of the performance of the polymers. The sol-gel reaction has been one of the most widely used approaches to prepare SiO₂, TiO₂ and other metallic oxides/polymer hybrid materials.

A new photosensitive polyimide/silica hybrid was prepared by sol-gel process in this study. The photosensitive polyimide (PI) was prepared from benzophenone - 3,3',4,4'-tetracarboxylic dianhydride (BTDA) and 4,4'-diamino-3,3'-dimethylidiphenyl methane (MMDA) by conventional solution polycondensation followed by a chemical imidization reaction.

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Tetraethoxysilane (TEOS) was then introduced to the PI solution followed by a hydrolysis process. The conventional photolithographic process includes the prebaking, exposure, development, fixing and finally hardening. In our study, a thermal gelation step is also required after the fixing to convert the hydrolyzed TEOS to silica network. The detailed photolithographic process used in this study is: prebaking at 100-110°C for 30 minutes, exposure with 300W high pressure mercury lamp for 8 minutes, development with 1,4-butyrolactone (GBL) for 40 seconds, fixing with NMP/isopropanol (1/4 by volume) and finally thermally treated at 110°C for 4 hours, 180°C for 2 hours, 220°C for 2 hours and 270°C for 2 hours. The preparation and photolithographic of PI/SiO₂ hybrids is described in Scheme 1.

Scheme 1. Preparation and photolithographic of PI/SiO₂ hybrids
Figure 1 is the results of atomic force microscopy (AFM) of pure PI and PI/SiO₂ hybrid with 10wt% silica content. Both PI/ SiO₂ hybrid and pure PI give good and similar patterns. This means that the introduction of silica and the gelation process do not seem to pose significant effect on the photolithographic properties of the PI film when the silica content ≤10wt%. While no satisfactory pattern can be obtained as the silica content is further increased.

The mechanical properties of the PI can also be effectively improved by the introduction of the nano-meter silica in Figure 2. In our study, it is remarkable to find that the tensile strength (failure) of the PI film is increased by 54% (from 61 MPa for the pure PI to 94 MPa for the hybrid) and, simultaneously, the elongation at break is increased by 63% (from 3.5% for the pure PI to 5.7% for the hybrid) when 10 wt% silica is introduced.

![SPM photograph of PI(a) and PI/SiO₂ (b) hybrid](image)

Fig. 1 SPM photograph of PI(a) and PI/SiO₂ (b) hybrid

The introduction of the nano-meter silica leads to significant improvements in the size stability and the thermal stability. Figure 3 is the relationship between the silica content and the thermal expansion coefficient (TEC) of the hybrid. The hybrid film containing 10 wt% silica has a coefficient of thermal expansion (CTE) measured by thermal mechanical analysis (TMA) of $45.7 \times 10^{-6} \text{ K}^{-1}$, about 25 % smaller than that of the pure PI ($65.9 \times 10^{-6} \text{ K}^{-1}$). The PI with a low CTE is extremely desired in microelectronic industry since the incompatibility between the high CTE of the PI and low CTE of the substrates, especially silicon chips, is
one of main causes of failure of the semiconductive devices. The initial thermal decomposition temperature (on-set temperature) assessed by thermal gravimetric analysis (TGA) is also increased by 18°C from 509.5°C for the pure PI to 527.5°C for the hybrid with 10wt% silica. The $T_g$ assessed by DSC is also increased with silica content was increased. (in Table 1).

![Graph 1](image1.png)

- tensile strength (Mpa)
- elongation at break (%)

Fig. 2 The mechanical properties of the hybrids

![Graph 2](image2.png)

Fig. 3 Relationship between silica content and thermal expansion coefficient of PI/silica hybrid films.

Table 1 Thermal Properties of PI/Silica Hybrid Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>PI</th>
<th>PI/Silica-5%</th>
<th>PI/Silica-10%</th>
<th>PI/Silica-20%</th>
<th>PI/silica-30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_d^a$ (°C)</td>
<td>509</td>
<td>516</td>
<td>528</td>
<td>532</td>
<td>527</td>
</tr>
<tr>
<td>$T_g^b$ (°C)</td>
<td>266</td>
<td>267</td>
<td>270</td>
<td>276</td>
<td>286</td>
</tr>
</tbody>
</table>

a Initial thermal decomposition temperature (onset temperature) determined by in TGA in $N_2$ and 20°C/min.
b Determined by DSC in 10°C/min.
References: