Overview of Photo-definable Benzocyclobutene Polymer

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Benzocyclobutene (BCB) polymer was developed at Dow Chemical in the late 1980's for microelectronics packaging and interconnect applications. Photo-definable BCB formulation was commercialized in 1994. The Dielectric polymer films produced from BCB formulations possess many desirable properties for microelectronic applications; for example, low dielectric constant and dissipation factor, low moisture absorption, rapid curing, and low temperature cure without generating by-products, minimum shrinkage in curing process, and no Cu migration issues. Derived from these properties, applications have been developed in: bumping/wafer level packaging, Ga/As chip ILD, optical waveguide, flat panel display, and lately in BCB-coated Cu foil for build-up board.

This article summaries the chemistry, the relevant properties and the typical process of photo-definable divinylsiloxane bisbenzocyclobutene (DVS-BCB) commercialized by Dow Chemical as CYCLOTENETM resin system.

Keywords : Cyclotene, benzocyclobutene, BCB

1. Introduction

Divinylsiloxane bisbenzocyclobutene (DVS-BCB, or BCB) polymer has been commercialized under the trade name Cyclotene™ by Dow Chemical, and has been widely used as a thin film dielectric in microelectronics applications in which low dielectric constant and low dissipation factor were required for improvement of the device performance. Dry etchable and photo-definable formulations are available as Cyclotene 3000 series and Cyclotene 4000 series, respectively.

Fig.1 Chemical Structure of DVS-BCB Monomer

2. Photo Cyclotene Polymer Properties

The Cyclotene 4000 series resins are I-line / G-line sensitive photo-polymers. These polymers are derived from B-staged DVS-BCB chemistry and have final film properties that are similar to the dry etchable Cyclotene 3000 series. Properties are shown in Tables 1 [11]. The Dielectric polymer films produced from BCB formulations possess many desirable properties for microelectronic applications; for example, low dielectric constant and dissipation factor, low moisture absorption, rapid curing, low temperature cure, and minimum shrinkage in curing process, and no Cu migration issues.

3. Outline of Photo BCB Polymer System

[ BCB polymer formulation]

Several formulations with different additive packages were developed for different film thickness targets. Photo-definable Cyclotene formulation consists of B-staged BCB polymer, photo-crosslinkers and other additives in mesitylene solvent. Optimization of B-staging polymerization degree and the photo-crosslinker package were the key parts of the formulation development.

[Development Solvent]

Unexposed area of the film can be developed. Selection of development solvent as well as the polymer formulation determines lithography performance. Organic development solvents, i.e. DS2100 for puddle development and DS3000 for immersion development are commercially available.

[Other Ancillary Chemicals]

Adhesion promoter coating prior to BCB polymer coating is recommended. The standard promoter is AP3000 (hydrolyzed acetoxy silane solution). Very thin film (<5nm) coating greatly enhances the adhesion of BCB to substrates [12].
Also, rework solvents for pre-exposed film, for post-exposed film, and for soft-cured film are available [13].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dielectric Constant (1 KHz-20GHz)</td>
<td>2.65 - 2.50</td>
</tr>
<tr>
<td>Dissipation Factor (1KHz-1MHz)</td>
<td>0.0008</td>
</tr>
<tr>
<td></td>
<td>(&lt; 0.002)</td>
</tr>
<tr>
<td>Breakdown Voltage (V/cm)</td>
<td>7 x 10^6</td>
</tr>
<tr>
<td>Volume Resistively (Ohm-cm)</td>
<td>1 x 10^19</td>
</tr>
<tr>
<td>CTE (ppm/°C)</td>
<td>52</td>
</tr>
<tr>
<td>Tg (°C)</td>
<td>&gt;350</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>87 ± 9</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>8 ± 2.5</td>
</tr>
<tr>
<td>Poisson Ratio</td>
<td>0.34</td>
</tr>
<tr>
<td>Residual Stress (MPa) On Si at 25°C</td>
<td>28 ± 2</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m°K) At 25°C</td>
<td>0.29</td>
</tr>
<tr>
<td>Water up-take (%) at 84%, 23°C</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Table 1
Properties of Thin Film of Cyclotene 4000 Series

4. Photo BCB Polymer Process

The proposed photo-BCB process flow is as follows:

1. Surface Clean
2. Adhesion Promoter coating
3. BCB Spin Coat
4. Pre-exposure Bake
5. Exposure
6. Pre-development Bake
7. Develop & Rinse & Dry
8. Post Development Bake
9. Cure
10. Plasma Descum

[Photo imaging]

Azide chemistry is used for photo-crosslinker system [14]. The bis-azide system was designed based on target thickness of spun film, photo-definability, sensitivity, latency under a certain storage conditions and miscibility to BCB polymer. Figure 2 shows the proposed reaction scheme of bis-azide with BCB prepolymer. The R-functionality in bis-azide structure determines the UV absorbance characteristics. Upon UV irradiation, reactive nitrene bi-radical (triplet excited state) is effectively generated with releasing nitrogen gas and undergoes addition reaction. Bis-azide is also thermally reactive to vinyl functionality.

![Proposed Azide Addition Reaction](image)

Figure 2 Proposed Azide Addition Reaction

In this article, Cyclotene 4024 (3 - 7 micron thick) and Cyclotene 4026 (7 - 15 micron thick) are discussed. UV/Visible absorbance spectra of Cyclotene 4024 are shown in Figure 3 as an example. Before exposure, photo-definable film absorbs highly at 365 nm. However, after light irradiation, the absorbance decrease at 365nm and increase at 405 nm and 436 nm wavelengths. The absorbance of the polymer at all three wavelength is further bleached during the final cure step of polymer. Consequently, the fully cured film is more transparent especially in visible light wavelength.

Cyclotene 4026 includes a different azide package that utilizes triplet state energy transfer mechanism within the azide system. Figure 4 shows the difference between Cyclotene 4024 and Cyclotene 4026 as a change in the percent transmittance at 365 nm and 405 nm for 5-micron thick film of both formulations as a function of exposure dose. Cyclotene 4024 has less transmittance than Cyclotene 4026 both at 405 nm and 365 nm. Therefore, thicker film can be photo-patterned with Cyclotene 4026 as a consequence of this increased transparency, i.e. light can penetrate through the film and crosslink the polymer at the bottom. Upon exposure, the photo-definable formulations both darken at 405 nm.
The recommended process includes a pre-development bake that should be done right before development process\[15\]. The purpose of the pre-development bake for BCB is to stabilize the development end-point. The development endpoint of BCB increases with time after coating, as shown in Figure 5. This is thought to be due to the uncurled polymer film become denser over the time, and as a result, penetration of the development solvent into the BCB polymer become slower. The pre-development bake process can restore the original density and thus the development solvent readily penetrates as before.

The puddle develop method consists of placing the exposed substrates onto the stationary chuck of the spin coater and dispensing a layer of DS2100 development solvent (puddle) on the surface. The DS2100 puddle is left on the polymer film for predetermined period of time to allow complete the dissolution of the non-exposed areas. The development time should be predetermined with an unexposed monitor wafer. At the end of the development period, the devices are rinsed by spinning at 500 rpm for 5 - 10 second, while a stream of DS2100 is dispensed onto the surface, followed by a 30 second spin dry at 3000- 5000 rpm. Finally, the wafer is baked on hot plate for 60 sec at 90 deg.C to thoroughly dry the film. The hot plate bake should be done without delay after development to prevent pattern distortion.

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[ Patterning by Development]
Immersion Development consists of placing the exposed substrates in a tank of warm DS3000 developer for 200% of predetermined development end point, typically 5 - 10 min for 5 - 10micron film. After the completion of development, the substrates are transferred to a cool DS3000 bath for rinse and quenching of the development. Typical temperature of the development bath is 30 - 40 °C and that of the cool bath is just the cleanroom temperature at which the development rate becomes very slow. Solubility of the unexposed area of BCB film has significant temperature-dependence.

[Thermal Cure]
After photo patterning process, the BCB has to be thermally cured to develop its full properties. BCB curing is a thermal process which does not need any catalyst and does not generate any by-product. As shown in Figure 6, the BCB four-member ring opens thermally to produce o-quinodimethane. This very reactive intermediate readily undergoes Diels-Alder reactions with vinyl functionality in DVS portion of BCB structure. Since the number of cyclobutene ring and vinyl functionality is stoichiometrically equivalent in the BCB molecule, a majority of the unsaturated bonds in the BCB polymer are consumed during thermal crosslinking.

Other additives in BCB formulation were selected from dienophilic materials that are integrated into polymer network upon cure.

Figure 6 BCB Thermal Crosslinking

The Cyclobutene ring is not reactive below the temperature of 175 °C, however, the polymer can be fully cured at 200 - 250 °C as shown in Figure 7. BCB polymer is typically cured in N2-purged oven. Soft cure (200 - 210 deg.C for 30 - 60 min) and Hard cure process (230 - 250 deg.C for 60 min) are suggested. The soft cure conditions leave 20 - 30 % cyclobutene ring unreacted, with which a subsequent layer of BCB react to give a monolithic structure.

The hard cure gives a fully cured BCB layer. As shown in Figure 7, BCB cure is rapid enough to use hot plate for cure as an alternative cure technique. Typical conditions of the hot plate cure is 300 - 320 deg.C for 30 - 60 seconds under inert gas atmosphere.

[ Plasma Descum]
After cure process, a plasma descum process is highly recommended to clean up via openings for high interconnect reliability. Since the BCB molecule contains silicon, a mixture of oxygen and fluorine containing gas such as CF4 should be used.

5. Lithographic Performance
The resolution is affected by various process parameters such as pre-bake conditions, exposure conditions and development conditions. [16][17]

[Pre-bake conditions]
Figure 8 shows the via bottom dimension versus mask dimension as a function of pre-bake temperature.

The optimized pre-bake conditions were proposed according to the pre-bake thickness, as described in the other publication[18][19]. Inappropriate conditions cause film quality problem during the development process such as cracking by over-bake, film lift-off by lack of bake.
Figure 8 Via Resolution vs. Prebake Temperature (90sec hot -plate bake) for 5-micron (Cyclotene 4024) and 10-micron Thick (Cyclotene 4026) Photo BCB, Without Pre-development Process

[Exposure dose]

Figure 9 shows the via bottom dimension versus the mask dimension as a function of exposure dose. Typically, lack of exposure causes problems such as film-lift off and wrinkling during the development process. Too much exposure may sacrifice the small-via resolution, although it is more dependent on the exposure tool performance or exposure gap.

Figure 9 Via Resolution vs. Exposure Dose for 5-micron (Cyclotene 4024) and 10-micron Thick (Cyclotene 406) Films of Photo-BCB Using Karl Suss MA-150 Exposure Tool (@10-micron Print Gap)
Without Pre-development Process

[Exposure gap]

Figure 10 shows the via bottom dimension vs. mask dimension as a function of exposure gap. Exposure gap influenced significantly on side-wall angle.

Figure 10 Via Resolution vs. Exposure Gap for 10-micron (Cyclotene 4026) and 5-micron Thick (Cyclotene 4024) Photo-BCB Using Karl Suss MA-150 Exposure Tool

Figure 11 shows the effect of exposure gap on side-wall angle.

Figure 11 Cross-sectioned Vias with Various Exposure Gap, 10-micron Thick BCB Developed by DS3000. Courtesy Fraunhoufer IZM Berlin Germany

<table>
<thead>
<tr>
<th>Photo</th>
<th>Exposure gap</th>
<th>Vis size</th>
<th>Side-wall Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0 micron</td>
<td>20 micron</td>
<td>80 degree</td>
</tr>
<tr>
<td>(b)</td>
<td>20 micron</td>
<td>30 micron</td>
<td>60 degree</td>
</tr>
<tr>
<td>(c)</td>
<td>40 micron</td>
<td>40 micron</td>
<td>40 degree</td>
</tr>
<tr>
<td>(d)</td>
<td>80 micron</td>
<td>80 micron</td>
<td>25 degree</td>
</tr>
</tbody>
</table>
Conclusion

BCB resin has inherently suitable characteristics to various microelectronics applications. Photo-definable BCB resin formulation (Cyclotene 4000 series) has been commercialized in several high volume consumer applications like wafer level packaging, GaAs telecom chips, high density / low loss printed wiring boards and flat panel displays.

Reference

[10] K.Ohba et al., " Development of CYCLOTENE Benzocyclobutene Polymer Coated Cu foil for Build-up Board Application" proc. IMT, Ohmiya, Japan, April 19-21,2000
[Other reference]