Development of Laser and Photodefinable Toughened Benzocyclobutene Dielectric Materials for 3D-TSV Integration

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Abstract

3D IC integration based on TSV technology has been recognized as a key enabler for next generation of electronic devices with reduced size factor and improved performances. The adoption of 3D-TSV technology also requires the development of innovative interconnect solutions that reduces the size of signal routing and therefore imposes new demands on dielectric materials used to isolate the copper interconnects. Benzocyclobutene polymers (Dow's CYCLOTENETM Advanced Electronic Resins) have been used to isolate copper interconnects in packaging applications for more than 20 years, due to a number of good attributes of the BCB polymer including low copper drift rate, low dielectric constant and low loss, low moisture absorption and proven reliability. However, the low fracture toughness and low elongation of BCB polymer has limited its use in stress buffer applications due to solder bump failure. Here we report the development of new laser and photodefinable toughened benzocyclobutene (BCB) dielectric materials that have following improved properties and benefits over commercial materials including: 1) Higher elongation to break at 25%, 2) Higher fracture toughness, 3) Improved lithographic performance, < 8µm minimal size feature, 4) Better stability, no change in Eo after 30 days at room temperature. The patterning and integration of these toughened benzocyclobutene materials and the processing conditions are also discussed. We believe this toughened BCB material will find wide applications as a stress buffer layer in 3-DIC.

Key words

Stress buffer layer, Patternable dielectric, Low copper drift, Benzocyclobutene

I. Introduction

Three-Dimensional Integrated Circuit (3D-IC) based on Through Silicon Via (TSV) technology has been recognized as one of the key enablers for improving device performance while reducing the power consumption and overall device package size to meet the needs of the next generation of electronic devices. The adoption of 3D-TSV technology also requires the development of innovative interconnect solutions that reduces the size of signal routing and therefore imposes new demands on dielectric materials used to isolate the copper interconnects. Benzocyclobutene polymers have been used to isolate copper interconnects in packaging applications for more than 20 years, due in large part to the very low copper drift rate for this polymer platform [1-4]. In addition, the BCB platform has a number of other attributes that make it attractive for new material development including low dielectric constant and low loss,

low moisture absorption, rapid low temperature curing without generation of by-products, minimum shrinkage in cure process and proven reliability [5-8]. However, the relatively low fracture toughness and low elongation of the BCB platform has limited its use in stress buffer applications due to solder bump failure during thermal cycle testing. Therefore it is highly desirable to improve the mechanical properties of the polymer platform while maintaining the good electrical and physical attributes of BCB polymer, enabling the development of both laser and photodefinable toughened BCB materials.

II. Overview of toughened BCB platform

Material properties of toughened BCB

Dow Electronic Materials (Dow EM) has developed a new toughened BCB polymer platform that serves as the basis

for both laser and photodefinable low-κ dielectrics for 3D IC integration applications. This new toughened BCB platform has significantly improved mechanical properties compared with 3000/4000 series dielectric materials.

Table I. Dielectric material property comparison

Material Property	Toughened BCB	CYCLOTENE 3000/4000	Polyimide	Epoxy / Phenol	Acrylic	Poly- benzoxazole
Cure Temperature (°C)	200-250	200-250	350	190	200	175-225
Tg / Dec. Temp (°C)	350	350	>350	210	180	240
Dielectric Constant	2.65	2.65	3.2	3.5	3.4	3.1
Dissipation Factor	0.002	0.001	0.002	0.02	0.03	0.009
CTE (ppm/K)	70	42	34	54	80	80
Tensile Strength (Mpa)	93	87	200	90	<50	170
Elongation	25%	8%	45%	7%	5%	80%
Residual Stress (Mpa)	24	28	34	<30	<30	25
Moisture Uptake	0.3%	0.2%	1.3%	1.5%	1.5%	0.5%

Data for toughened and standard BCB are the average of three values. Data for competitive materials are from the internet or technical papers. There is no guarantee by the authors that all data are correct.

Table I compares the material properties of the toughened BCB material with other commercial photodielectric materials after cure. BCB based materials are known in the industry to have very low dielectric constant and dissipation factor as well as very low moisture absorption. The new toughened BCB platform shows a three-fold increase in elongation to break, from 8 to 25%, and two-fold increase in $K_{\rm IC}$ fracture toughness, from 0.3-0.4 to 0.6-0.9 MPa m^{1/2} versus standard BCB. In addition, the residual stress of the toughened BCB platform is reduced from 28 to 24 MPa. Thus, the overall material properties for this toughened BCB platform are well-suited to stress buffer applications.

Lithographical performance of the photodefinable toughened BCB dielectric material

Several different photodefinable formulations have been developed to cover a range of film thickness from 1 µm to 15 µm similar to that of the CYCLOTENE 4000 series material. The new photodefinable toughened BCB is also negative tone and utilizes the same developer, DS2100, to remove the unexposed material. With this platform, we saw a significant improvement in lithographic performance relative to 4000 series as shown in Table II. The minimum feature size achieved for photodefinable toughened BCB was less than half of that for the 4000 series, yielding a 7 μm contact hole in a 6.5 μm thick film after soft bake. The film thickness after fully curing the dielectric material was 4.4 μm, corresponding to an aspect ratio of 1:1.6. Moreover, we have seen a significant increase in side wall angle ($45^{\circ} \rightarrow 85^{\circ}$) which allows for a reduction in pitch from 2:1 to <1.5:1 and therefore enables the fabrication of higher density lithographic patterns.

Table II. Lithographic property comparison of photodefinable toughened BCB material with 4000 series dielectric material.

	Photodefinable toughened BCB	CYCLOTENE 4000 Series		
Lithographic Properties				
Target Film Thickness Range	1-15 µm			
Tone	Negative			
Via Resolution/Feature Size	< 8 μm in 7.5 μm Film	20 μm		
Pitch	<1.5:1	2:1		
Aspect ratio	~1:1.6	1:3		
Wall slope	85°	45°		
Developer	DS2100 Solvent Type			
Edge Bead Solvent	T1100			
Stripper (Rework)	Primary Stripper A			

The lithographic resolution improvement of the toughened BCB platform over standard BCB was further shown by the cross-section SEM images of the printed vias as shown in Figure I. Wafers coated with toughened BCB were exposed using ASML 200 i-line stepper under recommended conditions. After development using and cure, the wafers were cleaved and cross section SEM images were taken. A $10~\mu m$ via opening with no observable residue using the toughened BCB material was achieved, while the smallest feature size that could be fully opened in 4000 series under similar film thickness and exposure conditions was $20~\mu m$.

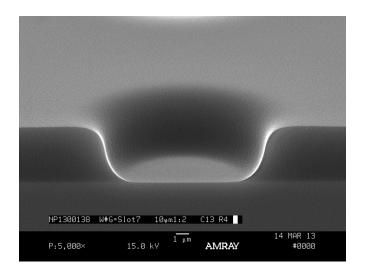


Figure I. Cross-section SEM image after development and soft cure of a 10 μm contact hole patterned with an ASML 200 i-line stepper on a 6.5 μm thick film after soft bake.

Laser ablation performance of the toughened BCB dielectric material

200mm wafers coated with 10.2 µm of toughened BCB were patterned using a 248 nm excimer laser stepper. The

trenches were patterned to a depth of 5-6 μ m while the vias were patterned through the entire dielectric thickness stopping on the silicon wafer. Representative images of the structures obtained are shown in Figures II, III and IV.

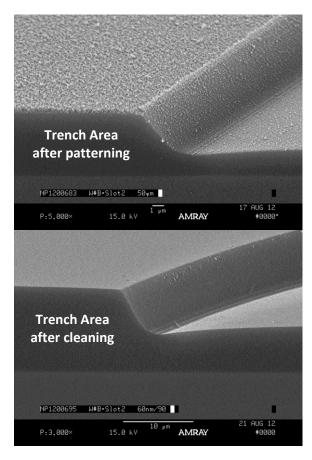


Figure II. SEM images of laser patterned toughened BCB before (top image) and after debris removal (bottom image).

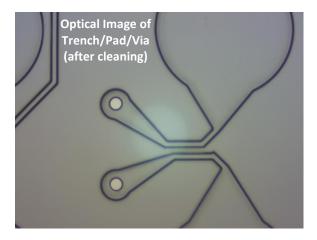


Figure III. Optical micrograph of dual layer via showing trench/pad/via structure patterned in a two-step process using an excimer laser stepper.

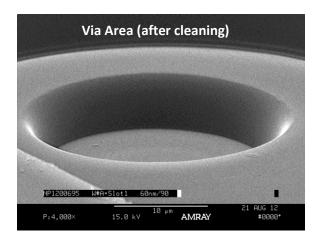


Figure IV. SEM images of dual layer via and trench/pad layer prepared using excimer laser stepper.

III. Lithographic processing conditions of the toughened BCB materials

A. Improved room Temperature Storage Stability

The photodefinable toughened BCB material has significantly improved thermal storage stability compared to CYCLOTENE 4000. The thickness and $E_{\rm gel}$ has less than 5% change after storing the materials at room temperature for up to one month.

B. Surface preparation and adhesion promotion

We recommend the use of AP9000S adhesion promoter for most wafer surfaces including BCB, silicon oxide, silicon nitride, silicon oxynitride, aluminum, copper, titanium and chromium. The use of an adhesion promoter is critical for passing the cross-hatch tape peel test after treatment of the dielectric under PCT conditions. The adhesion promoter was applied by dispensing statically or dynamically to cover the surface of the wafer. The wafer was then spun dry at 2000 rpm for 10-20 seconds followed by a baking of the adhesion promoter for 30 seconds at 90-150 °C.

C. BCB coating and soft bake

Toughened photo BCB was dispensed by spin coating onto the substrate shortly after the adhesion promoter application and also soft baked at 90°C for 90sec to remove solvent. The precise conditions used to deposit the resins (e.g. spin speed) would vary according to the final film thickness desired and which formulation was being used.

D. Exposure and post-exposure bake

After the soft bake, the substrates were cooled to room temperature before lithographic patterning. The exposure tools could be either i-line stepper or broad-band mask aligner. The photo-BCB film was given an exposure dose appropriate for the thickness of the film. After exposure, a

90°C post-exposure bake was needed to further cross-link the polymer.

E. Laser ablation and debris removal

Excimer laser ablation of toughened BCB films results in a moderate amount of debris re-deposited in the unexposed area. Although the residue could be removed with common organic solvents and semi-aqueous fluoride-based removers, the best results were obtained using a metal ion free developer, such as Dow's Microposit® MF CD-26 Developer

F. Development and post-development bake

Pattern development after exposure was accomplished by puddle development using DS2100 developer. Queue time prior to development was not critical. Delay time between exposure and development has been tested for up to 12 hours with no adverse effects. The wafer should be baked on a hot plate immediately after developing. This serves to further dry the film and to stabilize the via sidewall. The post-develop bake was carried out at 90°C for 60 seconds.

G. Cure and descum

After photolithographic processing, the film was cured in a N_2 oven. Since films of BCB resin are susceptible to oxidation at elevated temperatures, the film must be cured under an inert atmosphere at high temperature (recommended: <100 ppm of O_2 at >150°C). Two different cure profiles are commonly used: "soft" or partial cure (approximately 80% conversion) and "hard" or full cure (>95% conversion). In a box oven, a temperature of 200°C for 100 minutes was used for soft cure, and a temperature of 250°C for 60 minutes was used for hard cure.

Following cure the film was descummed by brief exposure to a plasma. A descum was necessary to remove a thin film of polymer residue left behind in the develop process. Since there is silicon in the BCB polymer, etching was done in $80:20 \ O_2/CF_4$ instead of pure O_2 .

V. Mechanical Property Measurements

A. Fracture toughness measurement

The plane strain fracture toughness, K_{1C} , was measured using single edge notched bend specimens measuring 3mm x 6mm x 30mm. Pre-cracking was done by insertion of a razor blade until a sharp crack had propagated to approximately half the specimen width. Specimens were loaded in three-point bending on a screw-driven load frame under a controlled displacement rate of 0.1 mm/sec. K_{1C} values were calculated using the peak load before fracture.

B. Elongation test

The elongation to break was measured with strip method (ASTM D5035). Cured strips measuring $10 \text{mm} \times 60 \text{ mm} \times 7 \text{ } \mu\text{m}$ was prepared by laser patterning of toughened BCB

that had been coated onto a copper wafer, followed by thermal curing and copper etching to release the strip. The strip was clamped with a gauge length of 25 mm (1 inch) and pulled in a tensile direction at 10 mm/min until break.

C. Residue stress measurement

The residue stress was measured with a Toho Flexus instrument. The wafer bow prior to BCB coating was first recorded. After BCB coating and curing, the wafer was remeasured for wafer bow. The residue stress was calculated based on wafer bow change before and after BCB application.

VI. Conclusion

In this paper, we have reported the development of a new laser and photodefinable toughened benzocyclobutene dielectric materials for 3D-TSV integration. The toughened BCB platform has a number of significantly improved lithographic and material properties over CYCLOTENE 3000/4000 series materials including: Three times the elongation to break, 25%, twice the fracture toughness, and improved lithographic performance with <8µm minimal size feature. The new platform also has significantly improved storage stability, with no change in Eo after 30 days at room temperature. We will continue to explore the use of toughened BCB materials as stress buffer layers in 3-D IC applications.

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