

Aqueous-Base-Developable Benzocyclobutene (BCB)-Based Material for Display Applications

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Abstract

A self-priming and photosensitive aqueous-base-developable benzocyclobutene (BCB)-based dielectric material curable in air is described. Patterned films have high resolution. Whether cured in nitrogen or in air, the formulation produces a film with optical, electrical, thermal, and mechanical properties desired for many microelectronic applications, such as a planarization layer or insulation layer in display applications. A self-priming, air-curable nonphoto-sensitive BCB material is also described.

1. Introduction

Polymeric dielectric materials play an indispensable role in microelectronics. They are used as passivation stress buffer layers for improved reliability and protection of semiconductor devices, dielectric layers in wafer-level chip-scale packaging, and planarization and insulation layers for display and optical applications.

Photosensitive benzocyclobutene (BCB)-based polymer has been widely used in packaging and bumping applications [1-5]. The monomer is divinylsiloxane-bisbenzocyclobutene (DVS-bisBCB). The formulation is negative-tone and requires an organic solvent as developer. In recent years, there has been a steady trend for photosensitive polymers to move from conventional solvent-developable formulations to aqueous-base-developable products [6]. The latter have the advantages of eliminating flammable organic solvents, better resolution, and environmental compatibility.

In this paper, we report a positive-tone, aqueous-base-developable BCB-based material which is a modification of the DVS-bisBCB polymer. A new monomer with a carboxylic acid group is incorporated into the BCB prepolymer to make it aqueous-base-soluble, and a photoactive compound, diazonaphthoquinone (DNQ), in the formulation makes it photosensitive. Thin films from these new BCB-based formulations have superior optical qualities and other excellent properties for display and packaging applications. A self-priming, air-curable nonphoto-sensitive DVS-bisBCB formulation is also described.

2. Results

Chemistry: Figure 1 shows the chemical structure of the two monomers and the partial structure of the prepolymer.

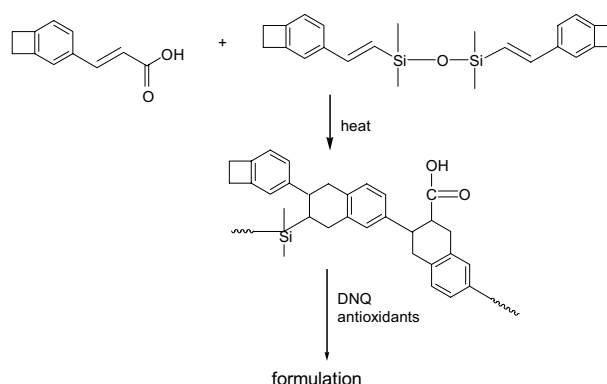


Figure 1. Chemistry of aqueous-base-developable BCB formulation.

Lithography: Dissolution rate of exposed and unexposed areas of a 3.9 μm , post-bake film with different development time is shown in Figure 2. Dissolution rate of exposed film shows good linearity. Unexposed film loss at end point was about 10%. Very good resolution was achieved and via shape was maintained after the patterned film was cured in air. Figure 3 shows a 5 μm via in a 2 μm film and a 5 μm via in a 4.5 μm film cured in air.

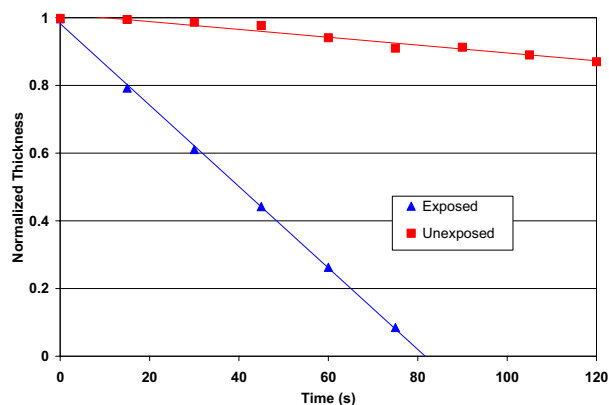


Figure 2. Dissolution rate of unexposed and exposed aqueous-base-developable BCB films.

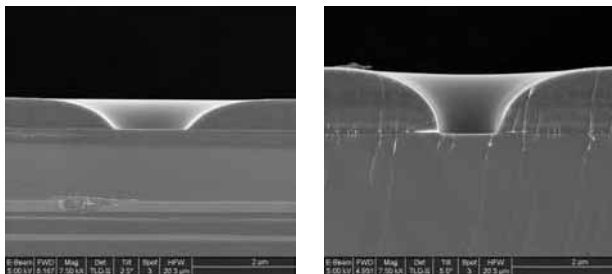


Figure 3. SEM of a 5 μm via in a 2 μm thick film (left) and a 5 μm via in a 4.5 μm thick film (right) cured in air.

Degree of Cure: BCB degree of cure was studied by the exothermic peak from BCB ring opening peaking at around 260°C. DSC of a film cured at 210°C for 90 min in air or in nitrogen showed a small exothermic peak of 18.5 J/g. Based on the DSC exothermic peaks of BCB-acrylic acid (1087 J/g) and DVS-bisBCB (916 J/g), degree of cure of aqueous-base-developable BCB at 210°C for 90 min was high. Fig. 4 shows the DSC plots of a film cured at 250°C for 60 min in nitrogen and a film cured at 210°C for 90 min in air. The film cured at 250°C for 60 min in nitrogen did not show an exothermic peak. A method to quantitatively monitor the degree of cure is under development.

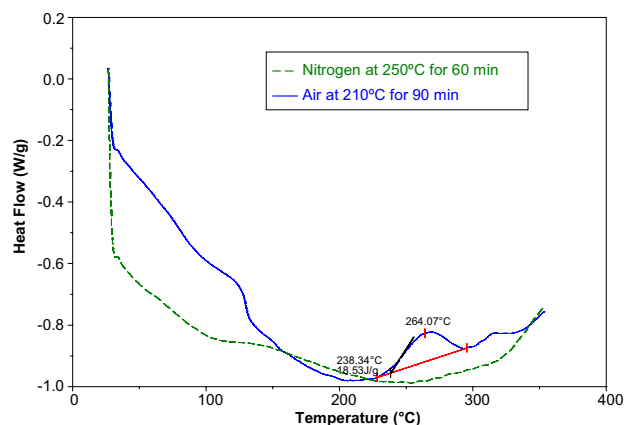


Figure 4. DSC plots of aqueous-base-developable BCB film cured under different conditions.

UV/Visible Spectroscopy: Flood exposure of the film before cure is recommended for high optical transmittance. Irradiation bleaches the film by converting the DNQ to indene carboxylic acid, which decarboxylates to form indene during cure [7]. Figure 5 shows the UV/visible spectra of a 2.8 μm thick film cured in nitrogen at 250°C for 60 min and a film with the same thickness cured in air at 210°C for 90 min on glass. At 400 nm, transmittance was 93% for the film cured in nitrogen and 90% for the film cured in air, respectively. Both samples had excellent and very comparable transmittance in the visible range between 400 nm and 700 nm. High optical transmittance of the polymer makes it an excellent material for display applications.

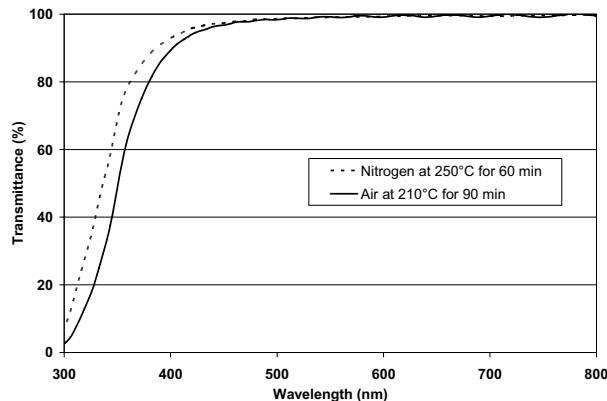


Figure 5. UV/visible spectra of an aqueous-base-developable film on glass cured under different conditions.

Properties: The electrical properties and water uptake data for aqueous-base-developable BCB cured in nitrogen and in air are listed in Table 1. Dielectric constant, dissipation factor, breakdown voltage, and water uptake of the polymer cured at the two different conditions are very similar. Water was depleted in about 2 min when the relative humidity (RH) was changed from 85% RH to 5% RH [8].

Table 1. Electrical properties and water uptake of aqueous-base-developable BCB film cured under different conditions.

Property	Cured in Nitrogen at 250°C for 60 min	Cured in Air at 210°C for 90 min
Dielectric constant	2.9	3.1
Dissipation factor	0.009	0.01
Breakdown voltage (MV/cm)	5.3	5.2
Water uptake at 50% RH (%)	1.2	1.3
Water uptake at 85% RH (%)	2.0	2.1

Table 2 shows the tensile properties of aqueous-base-developable BCB film cured in nitrogen and in air. Tensile strength and elongation at break of the film cured in nitrogen are about 20% and 40% higher than DVS-bisBCB-based polymer and comparable to aqueous-base-developable polyimides [9, 10]. Numbers for the air-cured sample are slightly lower.

Table 2. Tensile properties of aqueous-base-developable BCB film cured under different conditions.

Property	Cured in Nitrogen at 250°C for 60 min	Cured in Air at 210°C for 90 min
Tensile strength (MPa)	103	90
Tensile modulus (GPa)	3.6	3.7
Elongation at break (%)	11.2	10.6

Thermal mechanical analysis results of 10 μm thick, free-standing films of the base resin cured in air at 210°C for 90

min, the photo formulation cured in nitrogen at 250°C for 60 min, the photo formulation cured in air at 210°C for 90 min, and the photo formulation cured in nitrogen at 210°C for 90 min are shown in Figure 6. The four samples behaved very similarly in the studied temperature range. Coefficient of linear thermal expansion (CLTE) from 70°C to 150°C was 56 ppm per °C and 60 ppm per °C for a nitrogen-cured film and an air-cured sample, respectively. At 25°C, CLTE was 50 ppm per °C by data extrapolation.

The dynamic mechanical analysis (DMA) of 10 µm films cured in nitrogen (250°C for 60 min) and in air (210°C for 90 min) is shown in Figure 7. The polymer did not undergo any transition up to 350°C in either case.

Figure 8 shows isothermal thermal gravimetric analysis (TGA) of a 10 µm, free-standing film at three different temperatures. At 275°C, the polymer lost about 1.3 wt % per h, providing sufficient thermal stability for most microelectronic applications. The same formulation cured in nitrogen at 250°C for 60 min lost about 1 wt % per h at 275°C, which was slightly better [8].

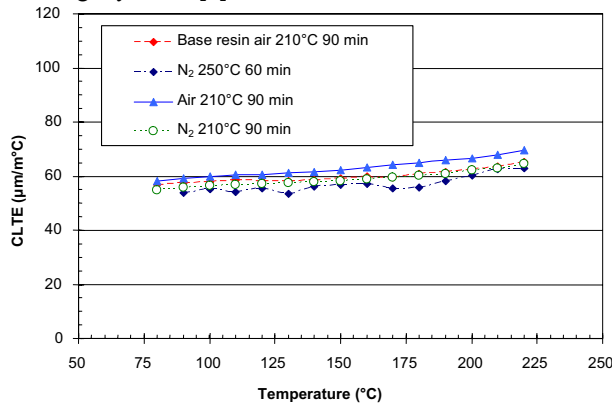


Figure 6. CLTE of aqueous-base-developable BCB films cured under different conditions.

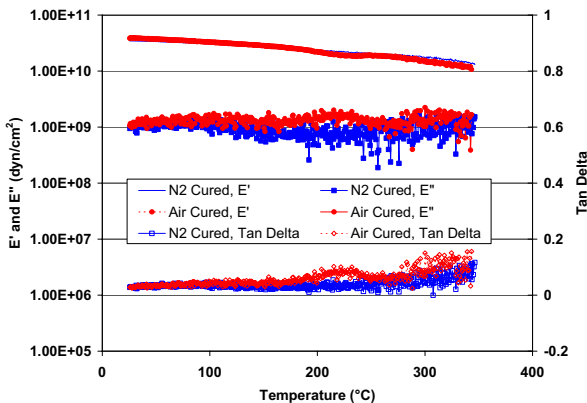


Figure 7. DMA of 10 µm thick aqueous-base-developable BCB film cured under different conditions.

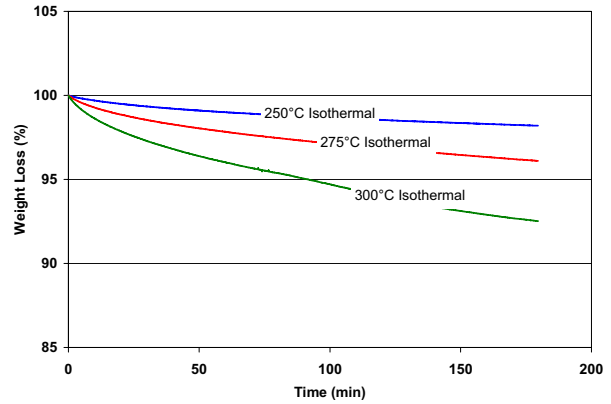


Figure 8. Isothermal TGA of 10 µm free-standing aqueous-base-developable BCB film cured in air at different temperatures.

Figure 9 illustrates the residual stress of aqueous-base-developable BCB film on 4 inch silicon wafers. The wafers were heated from room temperature to 250°C at 10°C/min and then cooled to -50°C. The linearity of the plot suggests that the polymer was in a glassy state in the studied temperature range. The heating curve and the cooling curve for the wafer cured at 250°C for 60 min were coincident. Residual stress at room temperature was 38 MPa. When the wafer cured at 210°C in air was heated to 250°C and then cooled down, the residual stress at a given temperature was slightly higher than that in the heating curve. The cooling curves of the wafer cured at 250°C in nitrogen and that of the wafer cured at 210°C in air are essentially identical. Heating the air-cured wafer at 250°C converted the residual BCB, and higher cure temperature resulted in higher residual stress.

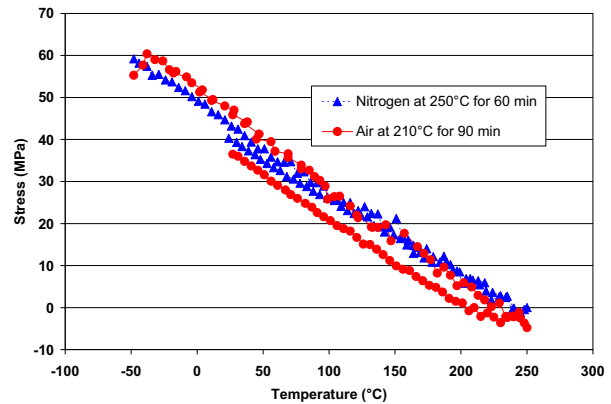


Figure 9. Residual stress of aqueous-base-developable BCB film on 4 inch silicon wafers cured under different conditions.

To determine adhesion properties of aqueous-base-developable BCB to different surfaces, the formulation was applied on wafers coated with Si, SiN_x, aluminum, copper, indium tin oxide (ITO), and soft cured aqueous-base-developable BCB film, and on glass wafers (Table 3). The wafers were placed in a pressure cooker at 121°C and 1 atm above atmospheric pressure at 100% RH for 48 h (JEDEC

22, Method A102B). Samples were evaluated by tape peel test (ASTM test D 3359). No detachment of aqueous-base-developable BCB from any of the surfaces was observed. Fracture toughness as measured by K1c numbers was generated by the modified edge lift-off test (m-ELT) [11], which also indicated good adhesion between aqueous-base-developable BCB and the surfaces. The formulation is self-priming and no separate adhesion promoter is needed.

Table 3. Adhesion properties of nitrogen-cured and air-cured aqueous-base-developable BCB film on different surfaces.

Surface	Cured in Nitrogen at 250°C for 60 min		Cured in Air at 210°C for 90 min	
	Tape peel after 48 h PCT ^a	m-ELT ^b (MPa√m)	Tape peel after 48 h PCT	m-ELT ^b (MPa√m)
Si	5B	0.38	5B	0.42 (ad fail)
SiNx	5B	0.43	5B	0.41 (ad fail)
Cu	5B	0.42	Cu oxidized	Cu oxidized
Al	5B	0.48	5B	0.35
ITO	5B	Not tested	5B	0.42
ITO	Not tested	Not tested	5B	0.42
Glass	5B	Not tested	5B	0.37
BCB ^c	5B	0.39	5B	0.40

^aPCT = pressure cooker test

^bFailure mode on wafer substrate except where specified

^cAqueous CB film on aqueous BCB film

To determine the adhesion properties of metals to aqueous-base-developable BCB film, a 200 nm thick layer of Al, Cr, or Ti was sputtered on top of a cured aqueous-base-developable BCB thin film. Samples were evaluated by a dry cross hatch tape peel test. No detachment of metal from the polymer was observed. The three metals adhere well to the polymer.

Chemical resistance of aqueous-base-developable BCB cured in nitrogen and cured in air was examined. Table 4 illustrates film thickness difference when a wafer was immersed in a solvent or TMAH for 10 min at room temperature. The nitrogen-cured film and the air-cured film showed good chemical resistance in common organic solvents except acetone.

Table 4. Resistance of aqueous-base-developable BCB film towards organic solvents and TMAH.

Solvent	Cured in Nitrogen at 250°C for 60 min		Cured in Air at 210°C for 90 min	
	Initial Film Thickness (μm)	Final Film Thickness (μm)	Initial Film Thickness (μm)	Final Film Thickness (μm)
Xylenes	3.629	3.629	3.458	3.456
Isopropyl alcohol	3.618	3.633	3.467	3.489
Acetone	3.621	3.798	3.540	3.679
N-methyl-2-pyrrolidinone	3.656	3.666	3.467	3.545
A 50:50 mixture of DMM and PGMEA	3.613	3.603	3.545	3.500
TMAH (2.35%)	3.650	3.624	3.475	3.575

Copper Migration Study: A 0.12 μm thick layer of aqueous-base-developable BCB was spin-coated on top of a 0.2 μm thick copper layer. The wafer was cured at 210°C for 90 min in nitrogen. Half of the wafer was further heated at 250°C for 90 min. The specimens were studied by XPS and results are shown in Table 5. Copper was not detected in the top ~ 10 nm of the polymer surface.

Table 5. XPS results from aqueous-base-developable BCB film in contact with copper before and after heat treatment.

	Wafer Cured in Nitrogen at 210°C for 90 min (atom %)	Cured Wafer plus Heat Treatment at 250°C for 90 min (atom %)
Cu (2p)	Not detected	Not detected
O (1s)	9.2	11.0
2σ	0.1	0.5
C (1s)	85.0	82.8
2σ	0.2	0.6
S (2p)	0.6	Not detected
2σ	0.0	
Si (2p)	5.2	6.2
2σ	0.2	0.2

The XPS information depth is 10 nm at 90° (estimated). The calculated detection limit of Cu (2p) was 100 ppm from 50 scans.

A sample with a 3 μm thick aqueous-base-developable BCB film on a copper-coated Si wafer was prepared and heat treated for 24 h at 250°C. A cross-sectional sample was made from each of the half wafers using a focused ion beam (FIB). The cross-sections were examined using transmission electron microscope (TEM) imaging and energy dispersive x-ray spectroscopy (EDS) to analyze for copper. EDS spectra were collected within 50 nm of the copper interface and approximately 250 nm from the copper interface and copper was not found.

Rework: Uncured aqueous-base-developable BCB prepolymer can be removed by flood exposure followed by rinse with TMAH. AZ EBR 70/30 (a mixture of 1-methoxy-2-propanol and PGMEA), di(propylene glycol) dimethyl ether (PROGLYDE DMM glycol diether), and methyl ethyl ketone (MEK) can also remove uncured prepolymer without flood exposure.

Other Studies: In a previous publication [8, 12], we demonstrated by XPS study that a descum process is not required for aqueous-base-developable BCB after patterning. Three layers of aqueous-base-developable BCB with copper pad has been built and it passed reliability tests.

Air-curable self-priming DVS-bisBCB-Based Polymer: DVS-bisBCB prepolymer has been formulated to allow the prepolymer to cure in air. This new formulation is also self-priming. Very low dielectric constant and water uptake, extremely high optical transmittance, and excellent degree of planarization are characteristics of this material (Table 6).

Table 6. Degree of cure and properties of the new DVS-bisBCB polymer formulation cured in nitrogen and in air.

Property	Nitrogen cure, 250°C, 1 h	Air cure, 210°C, 90 min
Degree of Cure (%)	98.6	95.2
Dielectric Constant	2.6	2.7
Breakdown voltage (MV/cm)	5.5	5.2
Water Uptake (%)	0.056 (50% RH) 0.10 (85% RH)	0.13 (50% RH) 0.23 (85% RH)
Transmittance at 400nm (%)	99	97

Figure 10 shows the UV/visible spectra of a 2.2 μm thick film cured in nitrogen at 250°C for 60 min and a film with the same thickness cured in air at 210°C for 90 min. At 400 nm, transmittance was 99% for the film cured in nitrogen and 97% for the film cured in air. Both samples had excellent and very comparable transmittance in the visible range between 400 nm and 700 nm. High transmittance of the polymer makes it an excellent material for display applications.

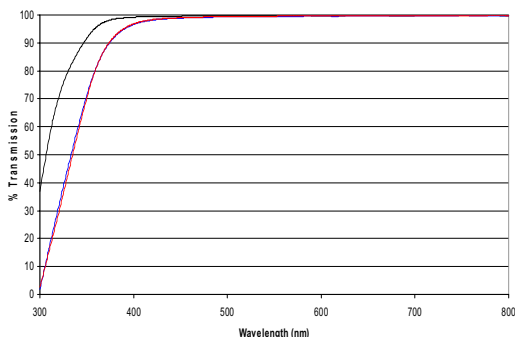


Figure 10. UV/visible spectra of DVS-bisBCB polymer cured in nitrogen and in air (2.2 μm film on quartz).

Figure 11 shows the isothermal thermal gravimetric analysis (TGA) of a 2 μm film on a silicon wafer. Temperature of the oven was maintained at 25°C for 120 min before it was ramped to 360°C at 20°C per min. After 20 min at 360°C, the polymer lost about 4% of its weight. This is the worst scenario since the oven temperature overshoot to 370°C. The polymer is reasonably stable even at 360°C.

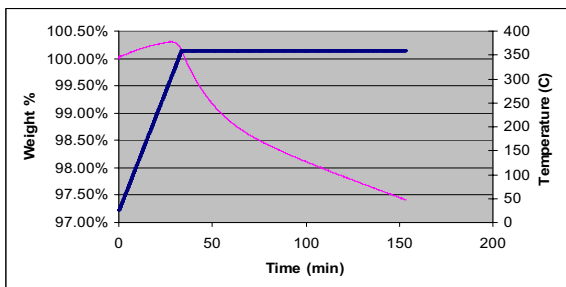


Figure 11. Isothermal TGA of a self-priming, air-curable DVS-bisBCB polymer at 360°C.

The new formulation is also self-priming, therefore potentially eliminating the need for separate operations to apply a primer. Cross-hatched tape peel tests conducted before and after 48 h in a steam pressure cooker at 121°C and 1 atm above atmospheric pressure at 100% RH (JEDEC 22, Method A102B) gave 5B ratings for thin films on Si, SiN_x, Al, Cu, indium tin oxide (ITO), and glass (meaning there were no areas of delamination).

3. Conclusion

Development of self-priming air-curable aqueous-base-developable BCB dielectric material is complete at The Dow Chemical Company. Thin films from the formulation show good dark erosion resistance. Lithography can be run on any resist line using tank development or spray developer tools similar to a standard resist process. The patterned film can be cured in nitrogen at 250°C for 60 min or in air at 210°C for 90 min. Curing is practically complete after 90 min at 210°C as judged by the good chemical resistance of the film. Resolution is excellent and vias are scum-free without an extra descum process. Films with very high transmittance are produced with flood exposure before cure. If low color is not a requirement, patterned films can be cured without flood exposure. The films have good electrical, thermal, adhesive, and mechanical properties, which are desirable for many microelectronic applications. DVS-bisBCB prepolymer is also formulated to become self-priming and air curable. The polymer has very low dielectric constant and water uptake, extremely high optical transmittance, and excellent degree of planarization.

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