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Aqueous-Base-Developable Benzocyclobutene (BCB)-Based Material – An Emerging Dielectric Material for Microelectronics

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A self-priming and photosensitive aqueous-base-developable benzocyclobutene (BCB)-based dielectric material curable in air is described. The polymer is made from divinylsiloxane benzocyclobutene and BCB-acrylic acid. Patterned films have high resolution, and via openings are scum-free without a descum operation. 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 packaging applications and a planarization layer or insulation layer in display applications.

Introduction

Polymeric permanent dielectric materials are used throughout the microelectronics industry. They are used as passivation stress buffer layers for improved reliability and protection of semiconductor devices, dielectric layers in wafer-level chip-scale packaging, integrated passives, MEMS fabrication and packaging and image sensor packaging, and planarization and insulation layers for display and optical applications.

One commercially important family of polymers in microelectronics is based on benzocyclobutene (BCB). Both photosensitive and nonphotosensitive divinylsiloxane bisBCB-based (DVS-bisBCB) products are commercially available from The Dow Chemical Company. Two of the key advantages of BCB-based polymers are that the curing process does not emit any volatiles and that the product from BCB ring-opening reactions are nonpolar hydrocarbon moieties. DVS-bisBCB polymer has very low dielectric constant and extremely low water uptake.

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

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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.

Experimental

Prepolymer and Formulation

2-Propenoic acid, 3-bicyclo[4.2.0]octa-1,3,5-trien-3-yl (hereinafter referred to as BCB-acrylic acid) was made from brominated BCB and acrylic acid by the Heck reaction (7). The prepolymer was made by heating a mixture of divinylsiloxane bisbenzocyclobutene (DVS-bisBCB) with BCB-acrylic acid in an organic solvent until the desired molecular weight was reached. The resin was then formulated with DNQ, which makes it photosensitive, a proprietary antioxidant that allows the prepolymer to be cured in air, and an adhesion promoter that makes the formulation self-priming.

Preparation of a 15 μm Film

A BCB prepolymer in a mixture of Proglyde DMM glycol diether and PGMEA (40% solids) was mixed with DNQ, antioxidant, and self-primer. Viscosity was 1990cPs. AP9000 was applied to wafer by spinning at 2000rpm followed by baking at 90°C for 60sec. Formulation was spread at 500 rpm for 10 sec followed by spinning at 1500rpm for 30 sec. The wafer was allowed to sit for 5 min before it was soft baked at 90°C for 2.75 min. Film surface was smooth before and after soft bake. If the wafer was bake immediately after spinning at 90°C with 1 min at proximity and 2.75 min contact, film surface looked like an orange peel after baking. Exposed dose was 800mJ/cm^2, and developed with 2.38% for 150sec. Film thickness after hard cure was 15.31μm with 10μm vias open.

Adhesion promoter AP9000 can be optionally used to widen the process window by spinning at 2000 rpm followed by baking at 90°C for 60sec prior to spin-coating BCB solution.

Property Measurement

Methods for property measurement have been reported in a previous publication (8).

Results and Discussion

Chemistry

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

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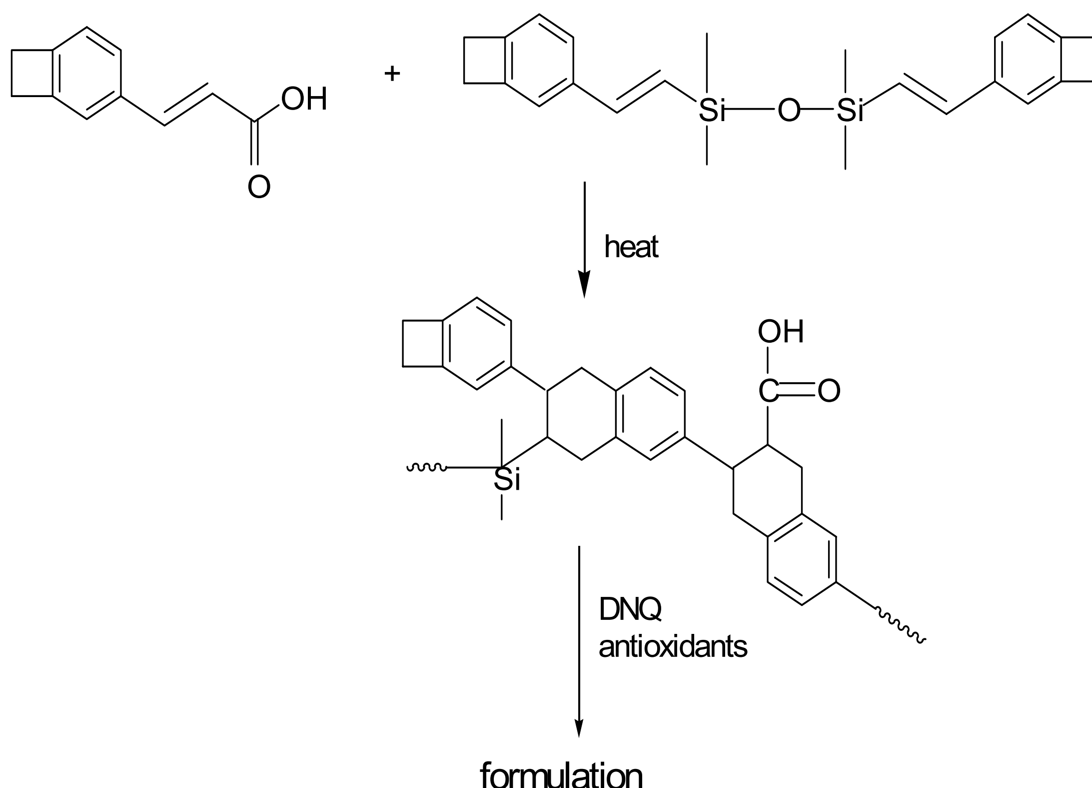

Figure 1. Chemistry of aqueous-base-developable BCB formulation.

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 3a through Figure 3c show a 2 μm via in a 1.6 μm film, a 10 μm via in a 1.6 μm film, and a 10 μm via in a 15 μm film. The 1.6 μm film was cured in air but the 15 μm film was cured in nitrogen.

Degree of Cure

BCB degree of cure was studied by the exothermic peak from BCB ring opening peaking at around 260°C. Differential scanning calorimeter (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.

Figure 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.

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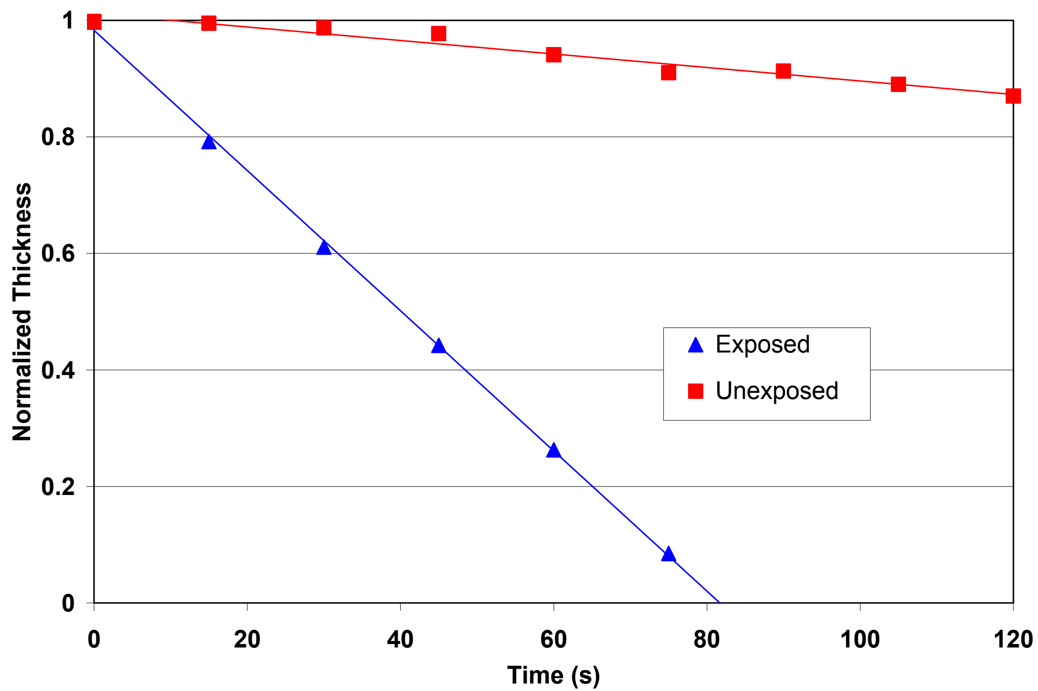

Figure 2. Dissolution rate of unexposed and exposed aqueous-base-developable BCB films.

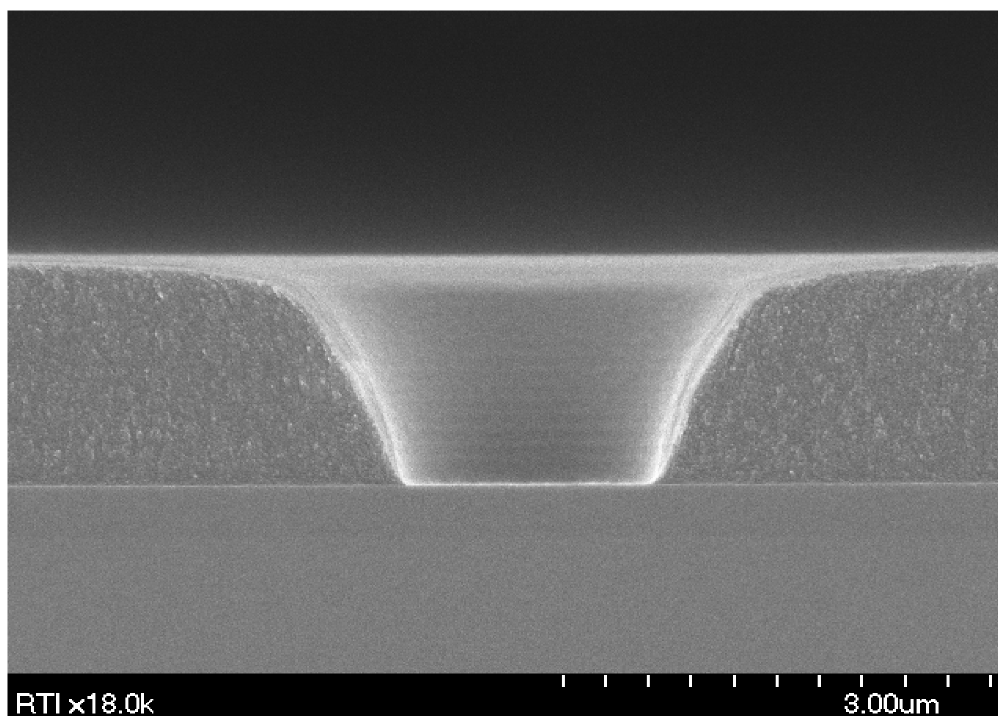

Figure 3a. SEM of a 2 μm via in a 1.6 μm thick film.

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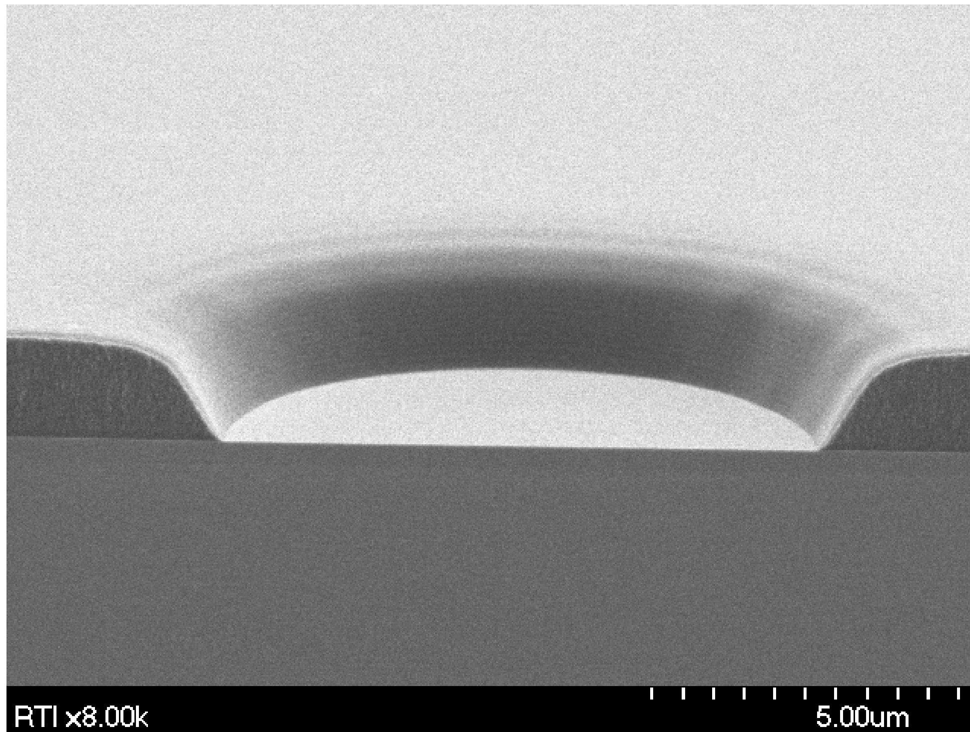

Figure 3b. SEM of a 10 μm via in a 1.6 μm thick film.

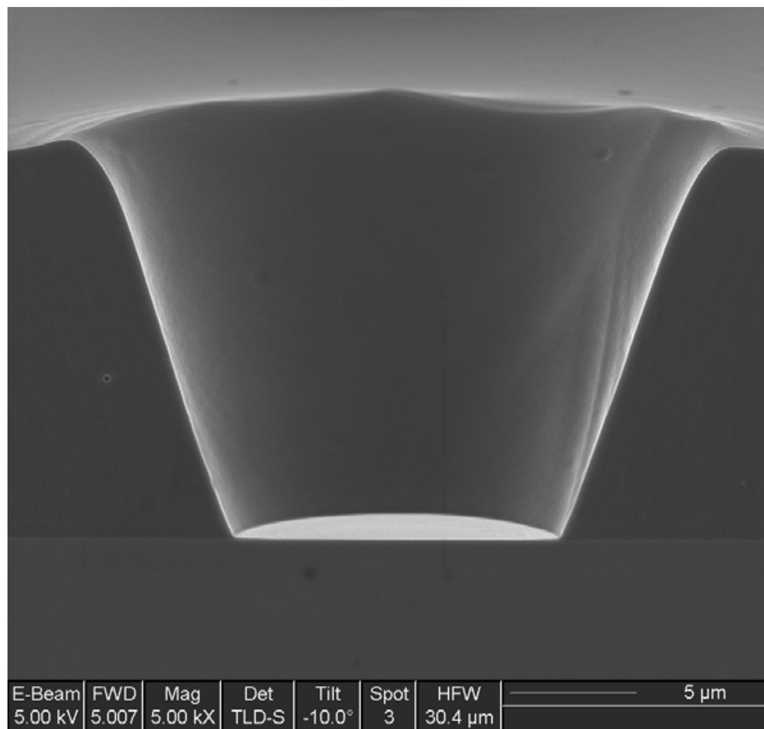

Figure 3c. SEM of a 10 μm via in a 15 μm thick film (right).

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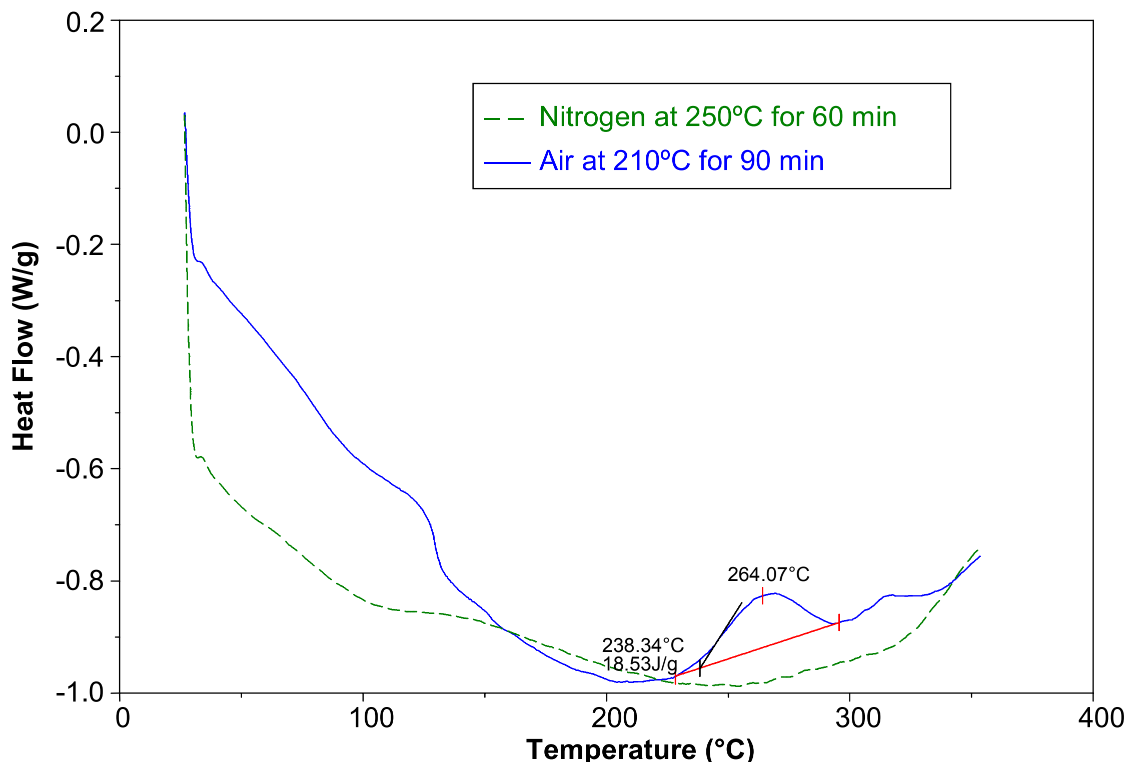

Figure 4. DSC plots of aqueous-base-developable BCB film cured under different conditions.

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 (9). 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.

Properties

The electrical properties and water uptake data for aqueous-base-developable BCB cured in nitrogen and in air are listed in Table I. 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 (10).

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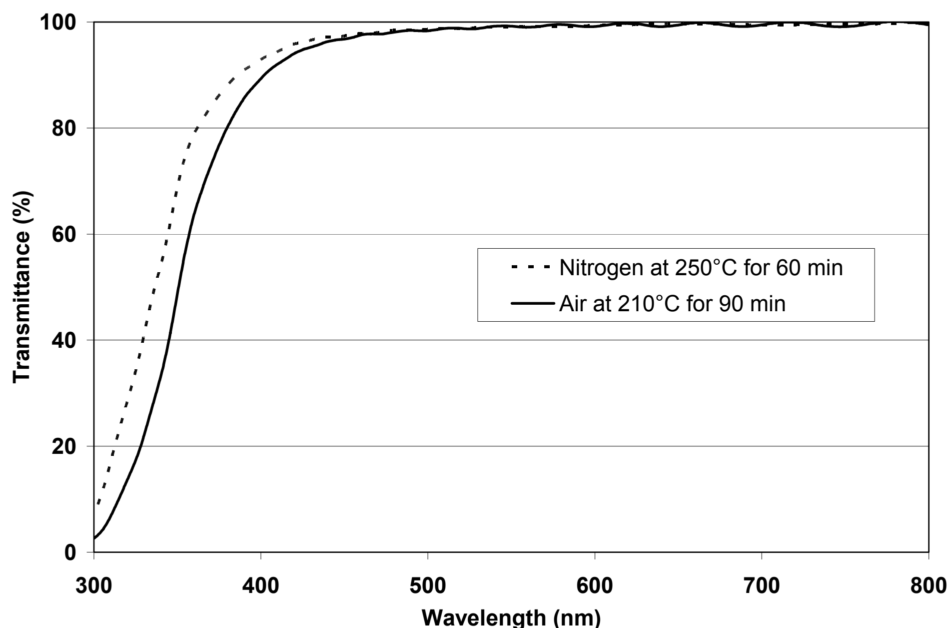

Figure 5. UV/visible spectra of an aqueous-base-developable film on glass cured under different conditions.

Table I. 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 II 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 (11,12). Numbers for the air-cured sample are slightly lower.

Table II. 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

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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.

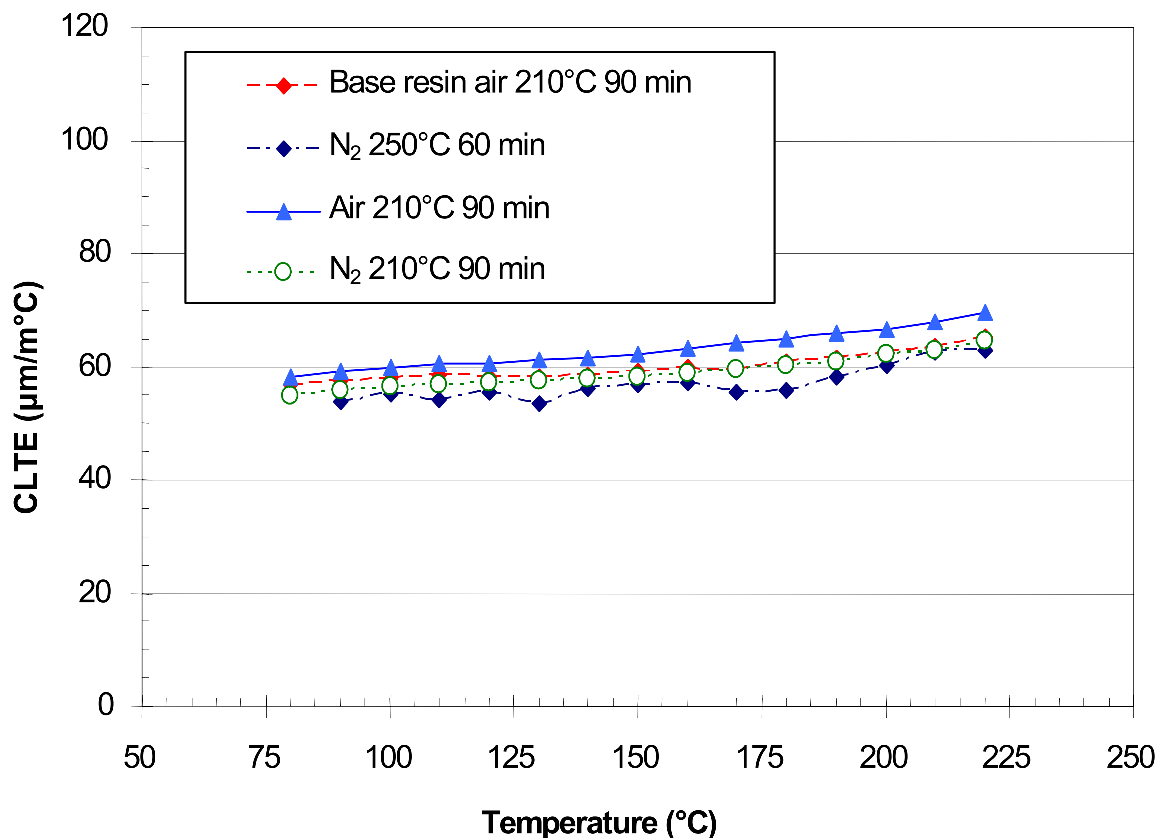

Figure 6. CLTE of aqueous-base-developable BCB films cured under different conditions.

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 (10).

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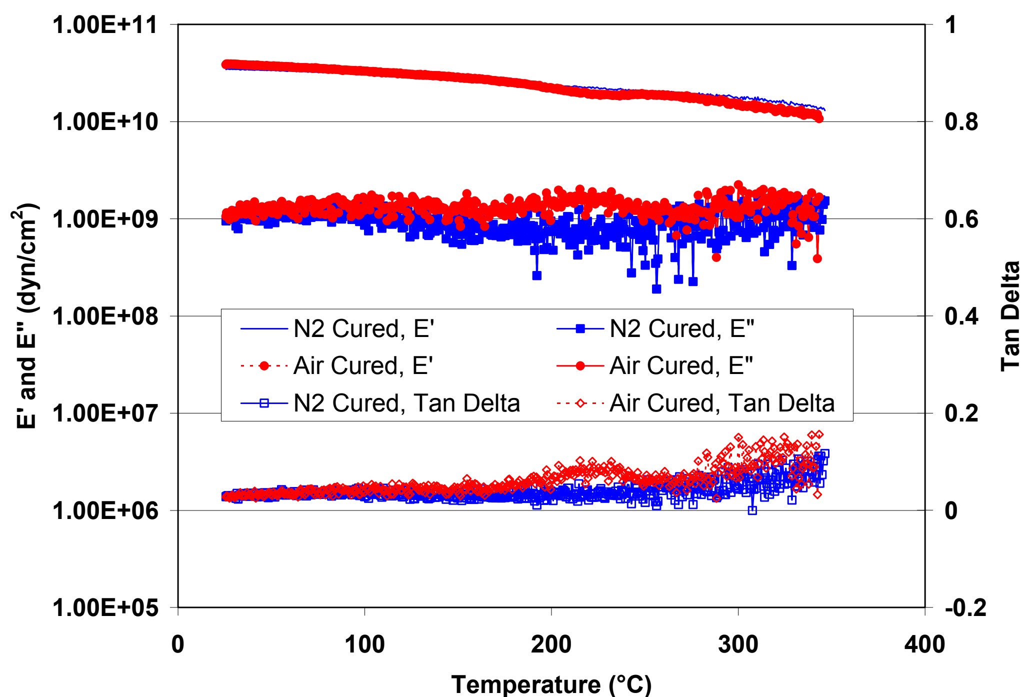

Figure 7. DMA of 10 μm thick aqueous-base-developable BCB film cured under different conditions.

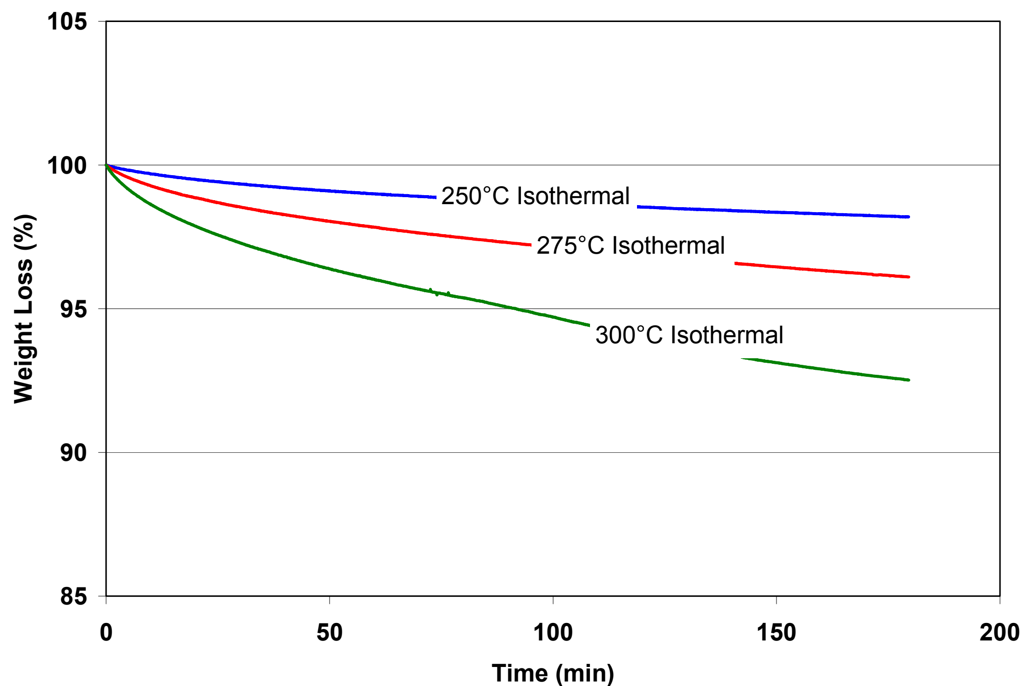

Figure 8. Isothermal TGA of 10 μm free-standing aqueous-base-developable BCB film cured in air at different temperatures.

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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.

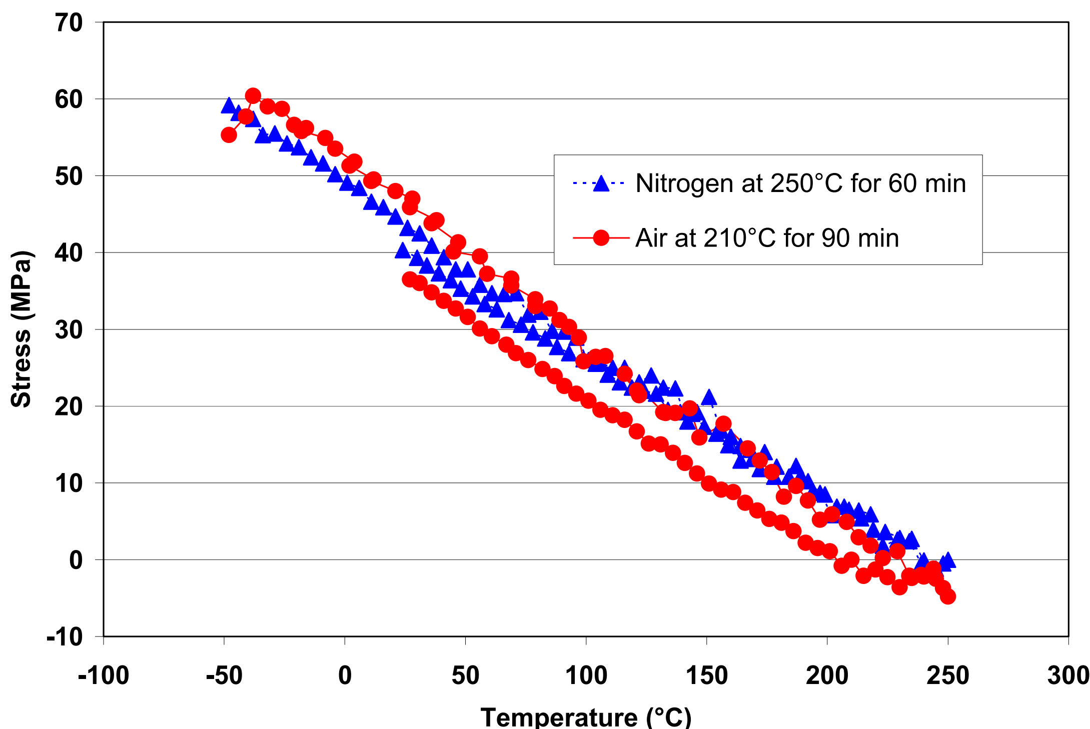

Figure 9. Residual stress of aqueous-base-developable BCB film on 4 inch silicon wafers cured under different conditions.

To determine adhesion properties of aqueous-base-developable BCB to different surfaces, the formulation was applied on wafers coated with Si, SiNx, aluminum, copper, indium tin oxide (ITO), and soft cured aqueous-base-developable BCB film, and on glass wafers (Table III). 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) (13), 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.

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

	Cured in Nitrogen at 250°C for 60 min		Cured in Air at 210°C for 90 min	
Surface	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

[a]PCT = pressure cooker test
[b]Failure mode on wafer substrate except where specified
[c]Aqueous 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 IV 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 IV. Resistance of aqueous-base-developable BCB film towards organic solvents and TMAH.

	Cured in Nitrogen at 250°C for 60 min		Cured in Air at 210°C for 90 min	
Solvent	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

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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 V. Copper was not detected in the top ~ 10 nm of the polymer surface.

Table V. 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.

Reliability Testing

A three-layer BCB with two-layer metal build-up was constructed to demonstrate multilayer aqueous-base-developable BCB and metal integration. Figures 10 and 11 show a schematic diagram and a scanning electron micrograph (SEM) of a build-up with three layers of aqueous-base-developable BCB and two layers of copper, respectively. Reliability tests were performed, and the multilayer build-up passed. Table VI shows testing conditions and results.

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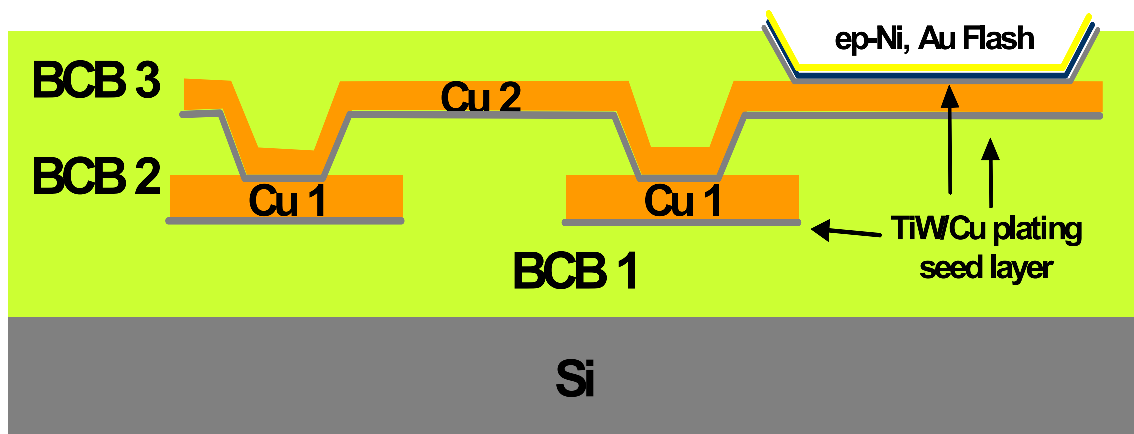

Figure 10. A schematic diagram with three layers of aqueous-base-developable BCB and two layers of copper.

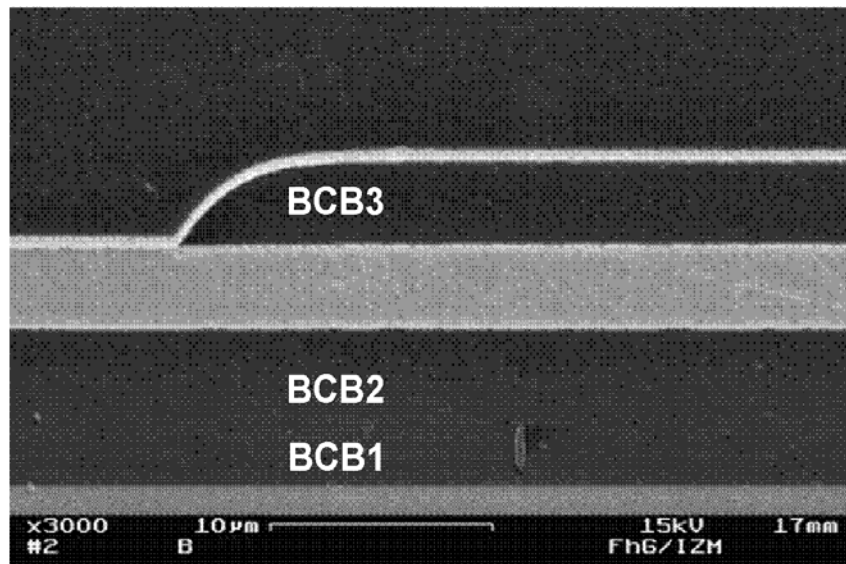

Figure 11. SEM of a build-up with three layers of aqueous-base-developable BCB and two layers of copper

Table VI. Reliability test conditions and results of buildups with three layers of aqueous-base-developable BCB and two layers of copper

Test Conditions	Hours or Cycles	Results
85°C/85% relative humidity	1000 hours	Resistivity change -1% to 0.8%, no via chain failure
Thermal storage at 150°C in air	1000 hours	Resistivity change -0.3% to 0.5%, no via chain failure
Thermal cycling (5 min RT, 10 min 125°C, 5 min RT, 10 min -55°C)	1000 cycles	Resistivity change -0.3% to 0.5%, no via chain failure

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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 previous publications (7,10), 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.

Conclusion

Self-priming air-curable aqueous-base-developable BCB dielectric material is a developmental product from 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.

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