CYCLOTENE ADVANCED ELECTRONICS RESINS

Processing Procedures for Dry-Etch CYCLOTENE Advanced Electronics Resins (Dry-Etch BCB)

1 Introduction

The 3000 series of dry-etch CYCLOTENE* Advanced Electronics Resins from The Dow Chemical Company are polymers which have been derived from B-staged bisbenzocyclobutene (BCB) monomers and developed for use in microelectronics applications. This Tech Note describes some of the general processing procedures used to coat and pattern these thin films, and lists many of the corresponding solution and film properties.

Thin films made of dry-etch CYCLOTENE Advanced Electronics Resins are ideal for those applications where a thin dielectric layer is required at the wafer level, or where a protective layer is needed for passivation or chemical resistance. Thin-film coatings of 1.0 to 26.0 µm are achievable in a single spin-coat application using standard IC processing techniques (see Table 1).

The dry-etch CYCLOTENE Advanced Electronics Resins are currently being used or considered within the electronics industry for many applications, including:

- multichip modules (e.g., MCM-D, MCM-LD, and MCM-CD),
- flat panel displays (e.g., planarization layers and high aperture dielectrics),
- interlayer dielectrics (e.g., silicon and GaAs),
- micro-machines (e.g., sensors and mechanical devices),
- optical interconnects (e.g., waveguides and switches),
- stress-buffer layers (e.g., logic, ASICs, and memory).

The dry-etch CYCLOTENE Advanced Electronics Resins have many properties which are highly attractive for these applications, including:

- low dielectric constant (2.65 which is essentially independent of temperature and frequency),
- simple and flexible processing scheme (using existing IC processing techniques),
- low level of ionics (ppm),
- low moisture uptake (0.25% at 85%RH),
- low cure temperatures (as low as 200°C in a couple of hours),
- rapid thermal curing (<1 min at 300°C and ~1 hour at 250°C),
- high optical transparency (>90% across the visible spectrum),
- high planarization level (>80% over 25 µm lines and spaces),
- high thermal stability (Tg > 350°C),
- high solvent resistance (highly stable to most organic solvents, bases, and aqueous acids),
- very low outgassing (undetectable below 300°C).

2 Storage

The 3000 series of dry-etch CYCLOTENE Advanced Electronics Resins should be stored at room temperature. The recommended shelf life for this product line is at least one year from the formulation information printed on the bottle label.

Table 1: Film Thickness Range of Dry-Etch CYCLOTENE Advanced Electronics Resins

Product	Film Thickness Range (µm) (spin coated @ 1000-5000 rpm)
CYCLOTENE 3022-35	1.0 - 2.4
CYCLOTENE 3022-46	2.4 - 5.8
CYCLOTENE 3022-57	5.7 - 15.6
CYCLOTENE 3022-63	9.5 - 26.0

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3 Processing Description

The following sections provide a general overview of the properties and processing procedures associated with dry-etch CYCLOTENE Advanced Electronics Resins. For more detailed information about processing options and variables, please refer to the literature references in Section 7 of this Tech Note, or contact a Dow representative at 517-636-5093. We can be contacted at our E-mail address: cyclotene@dow.com.

3.1 Surface Preparation

Substrates to be coated with one of the dry-etch CYCLOTENE resins should be free of all organic impurities and other contaminants prior to the coating application. Use of an adhesion promoter is highly recommended for many applications. A typical application procedure for adhesion promoter is outlined below:

1. Dispense Adhesion Promoter:
Dynamically dispense the adhesion promoter solution onto the center of the substrate while it is rotating at approximately 500 rpm (2-4 ml for a 6-inch substrate).

2. Spin Dry:
Spin the substrate at approximately 2000-3000 rpm for 20-30 seconds, or until dry.

Please refer to the Tech Note “Processing Procedures for Adhesion Promoters used with Photosensitive and Dry-Etch CYCLOTENE Advanced Electronics Resins,” (form number 618-00201) for more details about adhesion pro-moter selection, availability, and use.

3.2 Coating

Thin films made of dry-etch CYCLOTENE Advanced Electronics Resins are spin cast onto the substrate directly after adhesion promoter application. The precise conditions used to deposit the resins will vary depending on the final film thickness desired and on which formulation of the dry-etch CYCLOTENE Advanced Electronics Resin is being used (see Table 2).

A typical application procedure is outlined below:

1. Dispense Resin:
Begin rotating the substrate at a slow speed (50-100 rpm) and then dynamically dispense the dry-etch CYCLOTENE Advanced Electronics Resin onto the center of the substrate (approximately 2-3 ml for a 6-inch substrate).

2. Spread:
Increase the substrate speed to 500 rpm for approximately 6-10 seconds to spread the resin out from the center.

3. Spin:
Increase the substrate speed to a rate which is appropriate to achieve the desired coating thickness (1000-5000 rpm) for 20-30 seconds.

4. Edge Bead Removal:
Decrease the substrate speed to 600-1000 rpm and dispense a backside solvent (e.g.,T1100) for 5-10 seconds to remove any contamination from the backside and to remove the polymer which has formed at the edge. Increase the speed to 1500 rpm to dry the backside of the wafer.

Note: Other solvents such as cyclopentanone and xylene have also been observed to work well for backside rinse of the substrate after coating. Please refer to the Tech Note “Processing Procedures for Ancillary Chemicals used with Photosensitive and Dry-Etch CYCLOTENE Advanced Electronics Resins” (form number 618-00202) for more details.

Table 2: Typical Cured Thicknesses (μm) of Films made of Dry-Etch CYCLOTENE Advanced Electronics Resins

Spin Speed (RPM)	CYCLOTENE 3022-35	CYCLOTENE 3022-46	CYCLOTENE 3022-57	CYCLOTENE 3022-63
1000	2.4	5.8	15.6	26
2000	1.7	3.8	9.3	16
3000	1.3	3.0	7.3	13
4000	1.1	2.6	6.3	11
5000	1.0	2.4	5.7	9.5

3.3 Thermal Curing

After processing, the polymer films are cured to ensure resistance to subsequent processing operations, e.g. chemical baths, metallizations, and thermal cycling. This cure can be performed on a variety of tools, including: hotplate, convection oven, vacuum oven, tube furnace, or reflow belt furnace. The cure of films made of dry-etch CYCLOTENE resins must be carried out in the absence of oxygen (<100 ppm). This environment is easily achieved by flowing nitrogen through a convection oven, tube furnace, or by using a vacuum oven. These box oven cures typically take 4-5 hours to complete, including heat up and cool down. The use of a belt furnace is an attractive alternative to the box oven for many applications because the parts can be cured in a continuous process and then immediately sent on to the next operation. For high throughput applications, the cure can be sequentially performed on the track coater immediately after the development process. A hotplate temperature of approximately 300°C can be used to fully cure the dry-etch films made of CYCLOTENE in less than a minute.

It is suggested that the films made of dry-etch CYCLOTENE Advanced Electronics Resins be softcured between successive coats of the resin. The softcure procedure is used to enhance adhesion of subsequent layers deposited on top of the BCB film, including: metals, thin film polymers and molding compounds. It is recommended that the polymer reach 70-85% cure completion during the softcure process. An example of a softcure performed in a convection oven is provided in Table 3.

After all layers of polymer have been deposited, a final cure is often suggested (hardcure). The hardcure is typically carried out to achieve a 95-100% degree of polymer conversion. Hardcures are completed the same way as softcures, except that the cure time is longer and the temperature is higher. A typical cure profile to reach full cure (approximately 95% conversion) using a convection oven is given in Table 4.

Note: The multi-step heating sequence, as shown in Table 4, is incorporated simply to allow sufficient time for the oven to purge with nitrogen. If low oxygen levels can be achieved more quickly, the heating rate can be increased to match the purge level. A low oxygen level is only critical at temperatures above 150°C.

Table 3: Softcure Temperature Profile

Step 1	5 min. ramp to 50°C	5 min. soak
Step 2	15 min. ramp to 100°C	15 min. soak
Step 3	15 min. ramp to 150°C	15 min. soak
Step 4	60 min. ramp to 210°C	40 min. soak
Step 5	natural cool down	

Table 4: Hardcure Temperature Profile

Step 1	5 min. ramp to 50°C	5 min. soak
Step 2	15 min. ramp to 100°C	15 min. soak
Step 3	15 min. ramp to 150°C	15 min. soak
Step 4	60 min. ramp to 250°C	60 min. soak
Step 5	natural cool down	

3.4 Plasma Etching

Pattern definition of films made with dry-etch CYCLOTENE Advanced Electronics Resins is effectively accomplished by combining either a soft or hard mask process with a plasma process containing both oxygen and a fluorine-containing gas.

The soft mask process is accomplished by depositing a sacrificial photoresist layer on top of the dry-etch BCB film, patterning that resist layer using standard photoresist processing procedures, and then plasma etching to transfer the pattern in the photoresist mask through the film made of dry-etch CYCLOTENE. Varying the ratio between photoresist film thickness relative to dry-etch BCB film thickness can be performed to optimize the process for differential etch properties of each layer (resist versus dry-etch BCB).

Hard mask processes are often used for higher resolution work. The hard masks can be constructed of many materials (e.g. metal or inorganic oxide), as long as the materials are compatible with films made of dry-etch CYCLOTENE and a satisfactory differential etch rate exists between the hard mask material and the dry-etch BCB film. Common films used for hard masks construction include: copper, aluminum, or SiO_2. As in the case of the soft mask process, a plasma is used to transfer the pattern through the dry-etch BCB film. In soft and hard mask processes, the mask must be removed after the plasma etching is complete.

The plasma conditions used to etch films of the dry-etch CYCLOTENE Advanced Electronics Resins require a fluorine component in order to cleanly etch the Si chemical moiety which is present in the backbone of the dry-etch CYCLOTENE materials. Mixtures of SF_6/O_2, CF_4/O_2, or CHF_3/O_2 have been found to produce controlled etch rates greater than 1 μm per minute using parallel plate or RIE etchers. The absolute etch rate is a function of gas composition (e.g. CF_4 to O_2 ratio), system power, and chamber pressure. Pure oxygen plasmas (no fluorinated component in gas mixture) create an undesirable SiO_2 layer on the surface which often leads to a decrease in the apparent adhesion strength of layers deposited on top (polymer and metal).

In addition to the gas mixtures listed above, inert gases can also be added to the reactor to increase the overall pressure in the chamber and moderate the chemical vs. physical components of the plasma. Adding more inert gases to the reactor can lead to increased etch rates and affect sidewall profiles. Higher reactor pressures will produce feature sidewalls with a shallower angle. With the correct flourine content, higher pressures will also increase the etch rate of dry-etch BCB films. Higher power settings will typically etch faster and result in features with steeper sidewall angles. At low pressures, a higher flourine ratio is required to match the etch rates. For example, at one Torr, a good starting value is 10 to 15% fluorine-containing gas, and at 50 mTorr 20-25% fluorine may be required.

Another dry method for pattern formation in films made of dry-etch CYCLOTENE resins is to use scanning laser ablation. Both KrF (248 nm) and XeCl (308 nm) excimer lasers have been used to pattern films of the dry-etch CYCLOTENE resins. Depending on the fluence (100 to 2000 mJ/cm^2), ablation rates ranging from 0.15 to 0.35 μm per laser pulse were observed for cured films of dry-etch CYCLOTENE, using either laser. Please refer to the literature references in Section 7 of this Tech Note for more details on laser ablation and patterning.

4
Material Properties

The following three Tables list many of the solution and film properties of dry-etch CYCLOTENE Advanced Electronics Resins. Other properties can be obtained from several of the literature references in Section 7 of this Tech Note.

Table 5: Solution Properties of Dry-Etch CYCLOTENE Advanced Electronics Resins

Solution Properties	3022-35	3022-46	3022-57	3022-63
Solvent	Mesitylene	Mesitylene	Mesitylene	Mesitylene
Resin Content %	35	46	57	63
Viscosity (cSt @ 25°C)	14	52	259	870
Density (g/cc @ 25°C)	0.93	0.95	0.97	0.99

Table 6: Electrical Properties of Films made of Dry-Etch CYCLOTENE Advanced Electronics Resins

Property	Measured Value
Dielectric Constant (1 KHz)	2.65
Dissipation Factor (1 KHz)	0.0008
Breakdown Voltage (V/cm)	3.0×10^{6}
Volume Resistivity (ohm-cm)	1×10^{19}

Table 7: Mechanical Properties of Films made of Dry-Etch CYCLOTENE Advanced Electronics Resins

Property	Measured Value
Coefficient of Thermal Expansion (ppm/°C)	52
Glass Transition Temperature - Tg (°C)	>350
Tensile Modulus (Gpa)	2.0 ± 0.2
Tensile Strength (Mpa)	85 ± 9
Poisson’s Ratio	0.34
Elongation (%)	6 ± 2.5
Stress (Mpa)	28

5 Safety

The 3000 Series of dry-etch CYCLOTENE Advanced Electronics Resins must be used in a ventilated area. Inhalation may cause irritation of the upper respiratory passages and result in dizziness with anaesthetic effects. Direct exposure can cause eye damage and skin burns. In case of skin contact, flush with water and then wash thoroughly with soap and water. In case of eye contact, immediately flush eyes with water for 15 minutes. Consult a physician. Please read all warnings before use of the product.

6 Product Stewardship

The Dow Chemical Company encourages its customers and potential users of Dow products to review their applications of such products from the standpoint of human health and environmental quality. To help ensure that Dow products are not used in ways for which they are not tested or intended, Dow personnel will assist customers in dealing with environmental and product safety considerations. A Dow representative can arrange the proper contacts. Dow product literature, including Material Safety Data Sheets (MSDS), should be consulted prior to use of Dow products. These may be obtained from a Dow representative, by calling 1-800-441-4369 or (517) 636-5093; or by E-mail at cyclotene@dow.com.

7 Literature References

[1] T. Tessier & G. Chandler, “Compatibility of Common MCM-D Dielectric with Scanning Laser Ablation Via Generation Processes”, IEEE Transactions on CHMT, Vol. 16, No. 1, February 1993, pp. 39-45.

[2] B. Rogers, M. Berry, I. Turlik, P. Garrou, & D. Castillo, “Soft Mask for Via Patterning in Benzocyclobutene”, Proceedings ISHM/SPIE, Dallas, TX, Vol. 2105 November 1993, pp. 187-192.

[3] R. Sandell, G. Akerling, & A. Smith, “Multi-Chip Packaging For High Speed Superconducting Circuits”, IEEE Transactions on Applied Superconductivity, Vol. 5, No. 2, June 1995, pp. 3160-3163.

[4] Y. Lii & J. Wetzel, “Low Dielectric Dow CYCLOTENE 3022 (BCB) Etch for Multilevel Interconnection Integration”, Proceedings Electrochemical Society VLSI Science & Technology, 1995, pp. 266-274.

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[6] R. Shul, C. Sullivan, & G. McClellan, “Anistrotopic ECR Etching of Benzocyclobutene”, Electronics Letters, Vol. 31, No. 22, October 1996, pp. 1919-1921.

[7] V. Krishnamurthy, H. Cole, & T. Sitnik-Nieters, “Use of BCB in High Frequency MCM Interconnects”, IEEE Transactions on Components, Packaging, and Manufacturing Technology-Part B, Vol. 19, No. 1, February 1996, pp. 42-47.

8 Availability & Ordering Information

Dry-etch CYCLOTENE Advanced Electronics Resins are available in glass bottles from The Dow Chemical Company at the addresses given below.

The Dow Chemical Company also provides a full line of ancillary chemicals, adhesion promoters, development solvents and rework chemicals for use in conjunction with the dry-etch CYCLOTENE Advanced Electronics Resins. Please refer to these Tech Notes for more details about selection, availability, and use of CYCLOTENE Advanced Electronics Resins and related products.

Products	Available Sizes (grams)	
CYCLOTENE 3022-35 Advanced Electronics Resin	800	3500
CYCLOTENE 3022-46 Advanced Electronics Resin	800	3500
CYCLOTENE 3022-57 Advanced Electronics Resin	800	3500
CYCLOTENE 3022-63 Advanced Electronics Resin	800	3500

Form No.	Title
618-00199	Processing Procedures for Photosensitive CYCLOTENE Advanced Electronics Resins
618-00201	Processing Procedures for Adhesion Promoters used with Photosensitive and Dry-Etch CYCLOTENE Advanced Electronics Resins
618-00202	Processing Procedures for Ancillary Chemicals used with Photosensitive and Dry-Etch CYCLOTENE Advanced Electronics Resins
618-00203	Processing Procedures for Development Solvents used with Photosensitive CYCLOTENE Advanced Electronics Resins
618-00204	Processing Procedures for Stripping and/or Rework of Photosensitive CYCLOTENE Advanced Electronics Resins

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