Revised: March 2009

CYCLOTENE* 4000 Series Advanced Electronic Resins (Photo BCB)

Processing Procedures for CYCLOTENE 4000 Series Photo BCB Resins

DS3000 Immersion Develop Process

1. Introduction

The CYCLOTENE 4000 Series advanced electronic resins are I-line-, G-line-, and broad band-sensitive photopolymers that have been developed for use as dielectrics in thin film microelectronics applications. These polymers are derived from B-staged bisbenzocyclobutene (BCB) chemistry and have final film properties that are similar to the dry etchable 3000 series. Products are listed in Table 1. Properties of CYCLOTENE resins are shown in Tables 2-4 and Figure 1. Additional information on CYCLOTENE resins can be found on the web site, www.cyclotene.com

Table 1. Photo-BCB Formulations

CYCLOTENE resin	Viscosity (cSt)	Cured Thickness[1] (µm)
XUS35078 type 2	96	1.8 – 3.6
4022-25	34	0.8 – 1.8
4022-35	192	2.5 – 5.0
4024-40	350	3.5 – 7.5
4026-46	1100	7.0 – 14.0
XUS35078 type 3	1950	15 – 30

[1] Not to be construed as product specification

Table 2. Electrical and Thermal Properties of Photo-BCB (Cyclotene 4000 resin series)

Property	Value
Dielectric constant (1kHz – 20GHz)	2.65
Dissipation factor	0.0008
Breakdown voltage	5.3 MV/cm
Leakage current	4.7×10^{-10} A/cm^2 at 1.0 MV/cm
Volume resistivity	1×10^{19} Ω-cm
Thermal conductivity	0.29 W/m°K at 24°C
Thermal stability	1.7% weight loss per hour at 350°C

Table 3. Mechanical Properties of Photo-BCB (Cyclotene 4000 resin series)

Property	Value
CTE	42 ppm/°C at 25°C
Tg	>350°C
Tensile modulus	2.9 ± 0.2 GPa
Tensile strength	87 ± 9 MPa
Elongation at break	8 ± 2.5%
Poisson ratio	0.34
Stress on Si at 25°C	28 ± 2 MPa

1.1 Material Arrival and Storage

Photosensitive CYCLOTENE advanced electronic resins are shipped frozen in dry ice. If your shipment arrives with no dry ice and is warm, please contact your local Dow representative.

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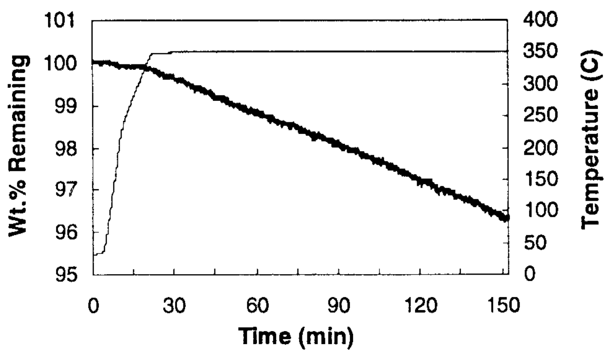
Table 4. Equilibrium wt % Water in Photo-BCB at Various RH at 23°C

CYCLOTENE resin	Film thickness (µm)	Relative Humidity (%) 30	54	84
4024-40	5	0.061	0.075	0.14
4026-46	10	0.058	0.077	0.14
4026-46	20	0.050	0.082	0.14

Table 5. Recommended Storage Temperatures and Times

Storage Need	Temperature	Shelf Life
Long term	Freezer (-15°C)	12-18 months from date of manufacture
Medium term	Refrigerator (4°C)	1-2 months
Short term	Clean room (20°C)	5-10 days

Figure 1. Weight loss from a 10µm film of Cyclotene 4026-46 resin by isothermal TGA under nitrogen at 350°C



Precipitation of photo additives can sometimes occur with CYCLOTENE 4022-35 resin, and occasionally with CYCLOTENE 4024-40. The additive readily re-dissolves upon warming to room temperature. Should this occur, some gentle mixing of the contents is desirable to ensure a homogeneous solution. See our application note on bottle rolling procedures for more information. An alternative is to remove the product from the dry ice and store it at -30°C to -40°C, as we have found that it is the transition from -78°C to -15°C that tends to initiate crystallization. Allowing the material to warm to room temperature before placing in the freezer also helps avoid precipitation.

1.2 Storage

As photosensitive CYCLOTENE resin ages, the spun-on thickness, and the develop end point, will gradually increase. The lifetime is based on the criterion of less than 5% change in thickness. Resins should be allowed to equilibrate to room temperature before use. Recommended storage conditions and times are shown in Table 5.

2. PROCESSING

Several process options are available, and are shown in Figure 2. Process A uses a hot plate soft bake and includes a develop end point monitor with each lot. Process B uses a hot plate soft bake and a pre-develop bake to stabilize the develop end point. (See below for further description of these process options.) An oven soft bake is also possible. The process that you choose is dependent on tool availability and manufacturability requirements.

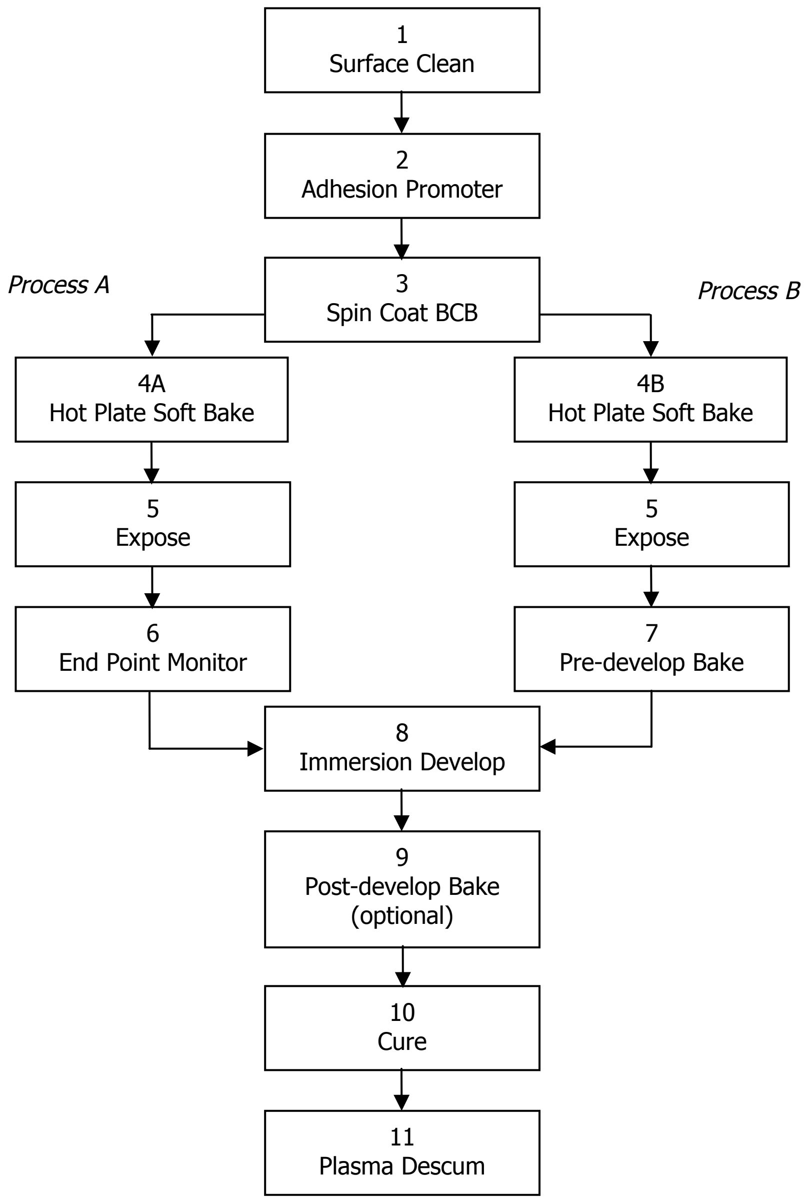
Step 1. Surface Preparation

Substrates to be coated with CYCLOTENE resin should be free of all organic impurities and other contaminations prior to coating. A clean surface is important to ensure good adhesion. An example of a cleaning procedure is an oxygen plasma clean, followed by dump rinse and spin-rinse dry.

Step 2. Adhesion Promoter

Adhesion promoter is recommended whenever the resin is to be adhered to any exposed metal or inorganic (silicon oxide, silicon nitride, alumina) surfaces. For example, we recommend

Figure 2. Process Flows for CYCLOTENE 4000 Series Advanced Electronic Resins



adhesion promoter application between multiple coatings of BCB if there is metal sandwiched between the two BCB layers. The recommended adhesion promoter is AP3000, which is an organosilane coupling agent in an organic solvent. It comes pre-mixed and does not require further mixing or dilution.

We recommend the use of AP3000 for most surfaces, including silicon dioxide, silicon nitride, silicon oxynitride, aluminum, copper, titanium and chromium.

Adhesion promoter is applied by dispensing statically or dynamically to cover the surface of the wafer. The wafer is then spun dry at 3000 rpm for 10-20 seconds.

Though often not required, the adhesion to surfaces such as silicon nitride, silicon oxide, copper, and aluminum, can be enhanced by baking the adhesion promoter for 30 seconds at 100 - 150°C, depending on surface, prior to BCB application. Please see our application note "Processing Procedures for BCB Adhesion" for more details on adhesion of BCB to various surfaces.

NOTE: Vapor prime adhesion promoters developed for photoresists (e.g., HMDS) do not work with the CYCLOTENE family of resins.

Step 3. BCB Coating

3.1 Equipment

It is recommended that coaters be equipped with two dispense heads (CYCLOTENE resin and adhesion promoter) backside rinse and EBR capability, hot plates and bowl exhaust.

3.2 Coating Process

Photo BCB films are spun onto the substrate directly after the adhesion promoter application and spin dry. The precise conditions used to deposit the resins (e.g. spin speed) will vary according to the final film thickness desired and which formulation of resin is being used. Table 6 shows thickness vs spin speed for CYCLOTENE 4022-35, 4024-40, and 4026-46 resins after soft bake (see section 4) and final thickness after exposure, development, and cure. Most of the loss in film thickness in the final, cured film occurs during the develop step. The loss in film thickness during the cure step (other than removal of residual developer solvent) is less than 5%. The thicknesses in Table 6 were determined using an open spin bowl. If a covered or closed cup coater is used, the thicknesses will differ and will depend on spin time as well as spin speed. Figure 3 shows a comparison of film thickness using open and closed bowl configurations.

Thicknesses of the XUS photosensitive products are shown in Table 7.

Final hard cured film thickness is also a function of subsequent processing steps, including soft bake conditions, exposure dose and development as explained in those sections below.

3.3 Dispense Resin

Dispense a puddle of resin of 1-5 ml (depending on topography, substrate size and resin viscosity) onto the center of the wafer. Either static or dynamic dispense (10-100 rpm) can be used. Alternatively, a reverse radial dispense can be used, which has been found to improve the material usage efficiency.

3.4 Spread

Increase the substrate speed to 500 rpm for about 5–10 seconds to spread the resin out from the center of the substrate.

3.5 Spin

Increase the substrate speed to a rate that will achieve the desired pre-exposure thickness (see Tables 6, 7). Backside rinse during spin of CYCLOTENE 4026-46 resin during the spin process will help suppress polymer filament ("cotton candy") formation.

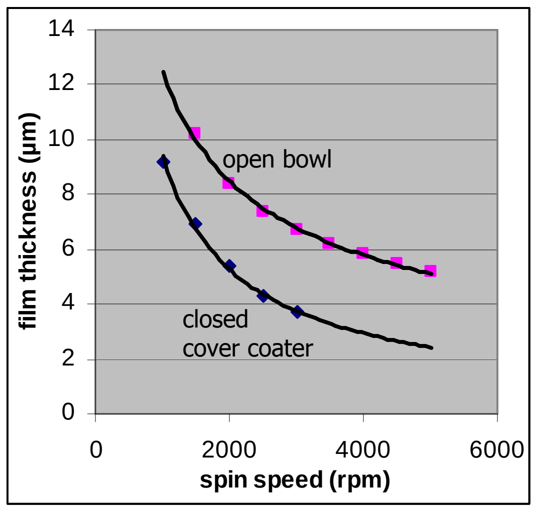
Table 6. Typical CYCLOTENE 4000 Series advanced electronic resin thicknesses after soft bake, and final thicknesses after full photo processing and hard cure (not to be construed as product specification).

	4022-35 thickness (µm)	4022-35 thickness (µm)		4024-40 thickness (µm)		4026-46 thickness (µm)	
Spin speed (rpm)	**After soft bake**	**After soft bake**	**Final thickness**	**After soft bake**	**Final thickness**	**After soft bake**	**Final thickness**
1500	2.4	6.9	5.2	10.2	7.2	18.5	14.2
2000	2.0	5.8	4.3	8.4	5.9	15.2	11.6
2500	1.83	5.2	3.8	7.4	5.2	13.3	10.2
3000	1.60	4.7	3.4	6.7	4.8	12.2	9.4
3500	1.41	3.1	6.2	4.4	4.4	11.3	8.7
4000		2.9	5.8	4.1	4.1	10.6	8.1
5000		2.6	5.2	3.7	3.7	9.4	7.3

Table 7. Thicknesses of XUS37078 photo-sensitive products after soft bake

Spin speed (rpm)	XU35078 type 2 thickness (µm)	XU35078 type 3 thickness (µm)
1000	6.22	37.3
1500	4.60	27.2
2000	3.90	21.3
2500	3.53	18.2
3000	3.11	15.8
3500	2.92	14.5
4000	2.72	13.4

Figure 3. Spin curves of CYCLOTENE 4024-40 resin in open and closed bowl configurations. Spin time was 30 seconds.



3.6 Edge bead removal and backside rinse

Decrease the substrate speed to 600-1000 rpm and dispense the backside solvent (T1100 Rinse Solvent) for 5-10 seconds to remove any contamination from the back side of the substrate and remove the "bead" that has formed on the front side edge. Increase the speed and spin for 10 seconds to dry (do not exceed the original spin speed). Top side edge bead removal can also be used, either from a dispense head on a track or manually with a syringe.

Step 4. Soft Bake
After spin coating, the films should be heated for a short period of time to drive out residual solvent. The specific time and temperature are dependent on the composition of the substrate as well as the thickness of the film. This can be done on a hot plate, in conjunction with a develop end point monitor (Step 4A) or in conjunction with a pre-develop bake (Step 4B). Either Step 4A or Step 4B is used and correspond to Process A and B in Figure 2, respectively. The soft bake is normally carried out immediately after spin coating.

If rework is needed after coat and soft bake, the film can be stripped with T1100 Rinse Solvent. Either a puddle process on a track or immersion in a tank can be used. DS3000 developer can also be used to remove an unexposed film.

Step 4A. Hotplate soft bake; develop end point monitor (Process A)
The recommended hot plate bake temperature depends on the thickness of the film after coat and bake. Recommended bake temperatures when using the end point monitor process are shown in Table 8. The end point monitor process is explained in more detail in Step 6. These are suggested guidelines; with the develop end point monitor process the soft bake temperature is not critical. The soft bake time and temperature will, however, have an effect on the subsequent processing. A higher soft bake temperature will lead to a longer develop time, a slight decrease in final film thickness, and a slight decrease in the amount of scum left behind after develop.

Step 4B. Hot plate soft bake, pre-develop bake process (Process B)
The recommended hot plate bake temperatures when using a pre-develop bake process (Step 7) are shown in Table 9. Bake temperatures higher than those indicated in Table 9, when used in conjunction with a pre-develop bake, can lead to cracking of the film.

Step 5. Exposure
Note that CYCLOTENE resins are negative acting, i.e., the exposed regions are crosslinked and will remain behind after development.

After the soft bake, the substrates should be cooled to room temperature before photolithography. The photo-BCB films should be given an exposure dose appropriate for the thickness of the film. Typical exposure doses for photo BCB films are given in Table 10. For example, a film of CYCLOTENE 4024-40 resin spun at 2500 rpm will have a thickness after soft bake of 7.4µm, thus, the recommended dose will be 25 $mJ/cm^2/\mu m$ x 7.4µm = 185 mJ/cm^2.

These doses were based on intensity measured at I-line and were determined on a proximity/contact aligner with broad-band exposure. Exposure dose and focus (gap setting for proximity printers, focal offset for steppers or projection printers) will have an effect on film quality, resolution, and sidewall slope. If exposure tools with only I-line or only G-line radiation are used (e.g., steppers), a higher exposure dose will be needed. Narrow band I-line steppers give good results with thin films (<5µm), but the process window becomes smaller as the thickness increases. On broad band steppers, G/H-line exposure is preferred, and I-line exposure is not recommended. Note that when the coating thickness varies due to topography on the wafer, the exposure dose should be based on the thickness of the thickest regions. Note also that these recommended doses were determined on silicon substrates. Re-optimization of the dose may be necessary based on substrate roughness and reflectivity (e.g., ceramic substrates, varying topology).

Exposure can be performed essentially immediately after soft bake, as soon as the wafer has cooled to room temperature. The delay time between soft bake and exposure can be at least 24 hours with no adverse effects. Slight film thickness drift, and CD loss, may be seen at longer delay times.

When fabricating multilayer devices, BCB is deposited on top of BCB. In these cases, higher exposure doses are often needed for the second and subsequent BCB layers, because of absorption of light by the underlying BCB and loss of reflected light. Insufficient exposure can lead to wrinkling of the film during the develop step.

Step 6. End Point Monitor (Process A)
If a pre-develop bake is not used, it is recommended that the end point time be established for each processing lot. The time can be determined by including a monitor substrate with the lot of substrates being processed. The monitor substrate is preferably a blank silicon wafer. This wafer is coated and baked identically to the other substrates, but should *not* be exposed. This wafer is developed as described in Step 8 below while looking for the time to endpoint. The end point "clearing" will show up as the end of a colored interference fringing pattern moving across the surface of the wafer. Without an end point monitor wafer (unexposed substrate), this effect is difficult or impossible to see on patterned and exposed substrates. The develop end point time will increase as the time delay between soft bake and develop increases.

Table 8. Hotplate soft bake temperatures for endpoint monitor process. All bakes are for 90 seconds.

CYCLOTENE resin pre-exposure thickness (μm)	Hot plate bake temp (°C)
<4.5	70
4.6 – 6.6	75
6.7 – 8.7	80
8.8 – 10.0	85
10.1 – 11.4	90
11.5 – 15.6	95
>15.6	100

Table 9. Hot plate soft bake temperatures for pre-develop bake process. All bakes are for 90 seconds.

CYCLOTENE resin pre-exposure thickness (μm)	Hot plate bake temp (°C)
<4.5	60
4.6 – 6.6	65
6.7 – 8.7	70
8.8 – 10.0	75
10.1 – 11.4	80
11.5 – 15.6	85
>15.6	90

Table 10. Exposure dose for CYCLOTENE 4000 series resins (broad band exposure, measured at I-line)

CYCLOTENE Resin	Exposure Dose (mJ / cm^2 per μm of pre-exposure film thickness)
4022-35	20 mJ/cm^2 per μm
4024-40	25 mJ/cm^2 per μm
4026-46	60 mJ/cm^2 per μm

Step 7. Pre-Develop Bake (Process B)
Before solvent development, an oven bake step can be added to stabilize the development end point time. Without this bake, the development end point time will increase as the film sits at room temperature, and is thus dependent on the time delay between process steps. The pre-develop bake will reset the develop end point to the same time, regardless of the time delay between soft bake and develop. The pre-develop bake must be carried out immediately before developing the wafer, otherwise the end point will again drift toward longer times. For films with a thickness of 3-10μm after soft bake, a 5 minute pre-develop bake of 55°C - 65°C in an oven is suggested. For thicknesses outside this range, please contact a Dow representative for suggested bake conditions. In addition to the time delay, the actual end point will be a function of film thickness, soft bake time and temperature, and developer temperature. For this reason a develop end point cannot be precisely defined here; each user will have to determine the end point at their facility on their tool set by developing at least one monitor substrate. A pre-develop bake will eliminate develop end point variation due to time delays. The user should realize that, in addition, the variables listed above need to be stable and controlled to achieve a uniform develop end point.

Step 8. Develop
Pattern development after exposure can be accomplished by puddle, immersion, or spray techniques. This processing guide is based on an immersion develop process. Please refer to "Processing Procedures for CYCLOTENE 4000 Series Photosensitive Resins (Puddle Develop)" for puddle development processing guidelines.

Immersion development uses DS3000 developer; puddle development uses DS2100 developer. These developers cannot be interchanged.

Develop can follow immediately after exposure; no wait time is needed. The delay time between exposure and develop can be at least 48 hours with no adverse effects. Some slight thickness drift, and CD loss, may be seen at longer delay times.

8.1 Safety and Handling

Advanced Developer DS3000 is composed of 1,3,5-triisopropylbenzene (CAS# 717-74-8). Its boiling point is 233°C and it has a flash point of 95°C and an autoignition temperature of 402°C. The Advanced Developer DS3000 should be stored at room temperature in sealed containers. Although DS3000 has a high flash point, preventive measures should be taken to avoid electrical discharges and ignition sources. Non-metallic develop tanks should be grounded. Refer to the Material Safety Data Sheet for further information on DS3000.

8.2 Process Equipment

The DS3000 develop process consists of three steps:

1) Develop in heated DS3000
2) Rinse in DS3000 at room temperature
3) Spin dry

The develop step should be run in a temperature-controlled tank with at least ±0.5°C temperature accuracy in the 30-40°C operating range. The develop tank should be installed inside a solvent wet bench with adequate ventilation. Additional developer circulation and filtration units are suggested for production processes. Ideal wet bench material of construction is stainless steel. A second bath with DS3000 at room temperature is recommended for stopping the develop process and rinsing the wafers. A suitable spin-rinse dryer (SRD) with heated nitrogen is needed to clean and dry the wafers and boat. Water rinsing in the SRD can also be done, and will assist in removing the high boiling developer solvent from the wafers.

8.3 Suggested Develop Procedure

For the chosen set of process parameters (film thickness, soft bake time and temperature, delay time between soft bake and develop), the develop time in DS3000 will depend on the bath temperature. At room temperature, develop time may be an hour or more, whereas, in the region of 30 to 35°C, the develop time is in the range of several minutes.

The process wafers are immersed in the heated DS3000 bath for a pre-determined length of time. If an end point monitor (Step 6) is included with the lot, this is used to determine the develop time. The total develop time should be about 150% to 200% of the end point (i.e., overdevelop by 50% to 100%). Tests at various sites indicate that bath life is in excess of 200 wafers (200 mm) per gallon of DS3000 developer. An example of a DS3000 immersion tank is shown in Figure 4.

After this develop step, the boat of wafers is agitated for 1-2 minutes in the second DS3000 bath which is kept at room temperature. This step is done to stop the develop process, to dilute the BCB-loaded developer from the first tank, and to clean the wafers with fresh developer before moving to the drying step.

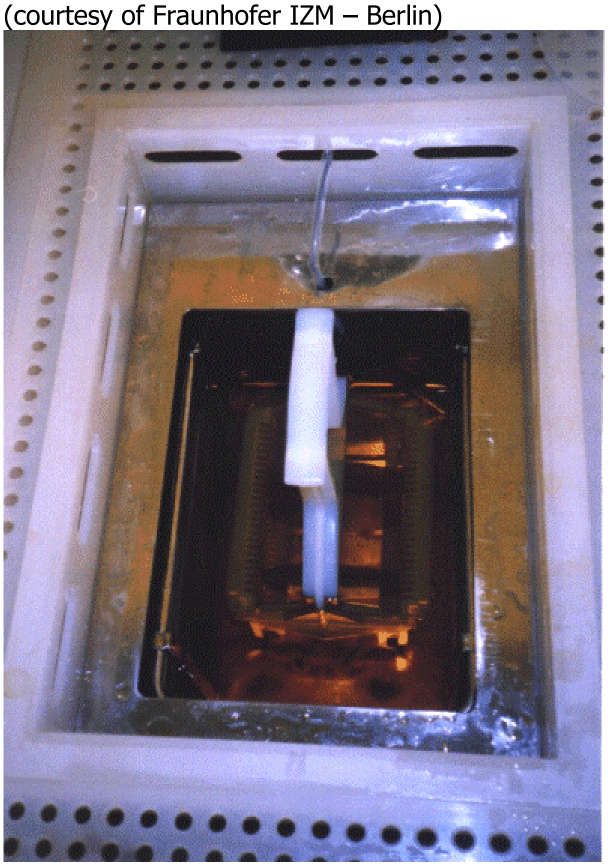
The final step consists of drying the wafers in a spin-rinse-dryer (SRD). Ideally, this tool should be located close to the developer baths. Its drain and exhaust should be connected to the solvent extraction and solvent waste system.

The nitrogen should be heated to improve the drying effect while spinning. A program that was shown to be effective was a 1-2 minute spin at 1000-2000 rpm and a 5-10 minute spin at 500-800 rpm with warm nitrogen blow. Alternatively, a standard SRD program (DI water spray clean with subsequent nitrogen and spin dry) can be used. Check with your safety and engineering department for equipment compatibility with DS3000.

8.4 Rework

Once the film is exposed, it is insoluble in most solvents. Exposed and developed films can be reworked by stripping in Primary Stripper A. The wafer is immersed in the stripper bath for 30 minutes at room temperature or for 5 minutes at 80°C. This is followed by a rinse in IPA and a water rinse. The stripper absorbs atmospheric moisture at room temperature, which inactivates the bath and makes it corrosive to metals. Use at 80°C is recommended because the bath remains dry at this temperature. If the stripper is to be used at room temperature, it is recommended that only a freshly poured bath be used, and that the chemical not be re-used. See "Rework Procedures for CYCLOTENE 3000 Series and 4000 Series Resins" for more details.

Figure 4. Heated DS3000 Immersion Tank (courtesy of Fraunhofer IZM – Berlin)



Step 9. Post-Develop Bake
For optical inspection after development, a one minute bake at 80°C – 100°C is suggested.

Step 10. Cure
After photolithographic processing is complete, the film is cured. A variety of equipment can be used for curing CYCLOTENE resins, such as a box oven, belt furnace, tube furnace, and hot plate. Except for early out-gassing of residual solvent, CYCLOTENE resins do not evolve volatiles during cure, and, thus, there are no constraints on the heating rate. The only requirement is that, since films of CYCLOTENE resin are susceptible to oxidation at elevated temperatures, the film must be under an inert atmosphere at high temperature (recommended: <100 ppm of O_2 at >150°C). Please refer to "Cure and Oxidation Measurements for CYCLOTENE Advanced Electronic Resins". Thus, the maximum oven ramp rate depends on how rapidly the oven can be purged of oxygen. The extent of cure is a function of time and temperature, as shown in Figure 5.

Two different cure profiles are commonly used: "soft" or partial cure (approximately 80% conversion) and "hard" or full cure (>95% conversion). Soft cure is used for lower BCB layers when multiple BCB layers are used in a structure; it provides improved adhesion between the polymer layers. Hard cure is used when one layer is used, or for the last layer in a multi-layer build. It gives the film maximum chemical resistance and stable mechanical and electrical properties. In a box oven, a temperature of 210°C for 40 minutes is used for soft cure, and a temperature of 250°C for 60 minutes is used for hard cure. Recommended cure profiles are shown in Table 11.

The time delay between develop and cure can be up to 4 days with no adverse effects. Some slight change in via resolution may be seen with longer delays. The cure delay time does not affect film thickness or adhesion.

Step 11. Descum
Following cure the film is descummed by brief exposure to a plasma. A descum is necessary to remove a thin film of polymer residue left behind in the develop process. This residue is typically less than 1000Å thick, hence, a descum process which removes 1000 - 2000Å of polymer is generally sufficient. Best results are obtained with a parallel plate reactive ion etcher. Isotropic downstream etchers can also be used. Barrel etchers give poor etch uniformity and are not recommended. Since there is silicon in the BCB polymer, etching cannot be done in pure O_2; some fluorine is needed in the etch gas mixture. A typical etch gas is 80:20 O_2/CF_4; this

provides a good balance of organic etching by O_2 and silicon etching by CF_4. SF_6 (90:10 O_2/SF_6), or other fluorine sources such as NF_3, can be used instead of CF_4 with good results. Lower concentrations of CF_4 will reduce the silicon etch rate and can lead to an undesirable build-up of a thin layer of amorphous SiO_2 on the surface of the BCB film. This can result in BCB cracking, as well as poor adhesion of materials deposited onto the BCB film.

An O_2/CF_4 or O_2/SF_6 plasma will cause corrosion of copper. If copper metal is exposed during the descum, a 30 second dip in 10% acetic acid is necessary immediately after the descum to prevent corrosion and discoloration of the copper surface.

Figure 5. BCB % cure vs time and temperature

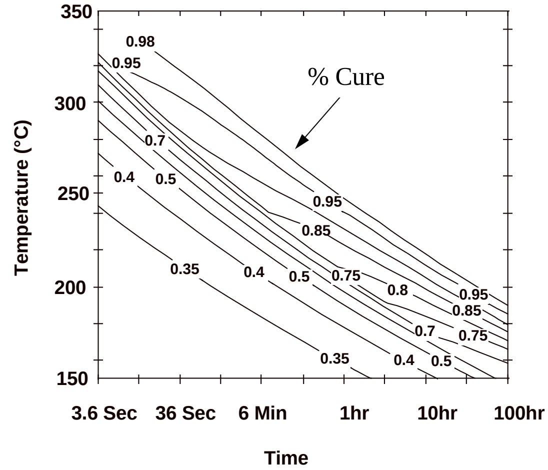


Table 11. Profiles for convection oven curing

step	soft cure	hard cure
1	15 min ramp to 150°C	15 min ramp to 150°C
2	15 min soak at 150°C	15 min soak at 150°C
3	ramp to 210°C	ramp to 250°C
4	40 min soak at 210°C	60 min soak at 250°C
5	cool to <150°C	cool to <150°C