Revised: April 2008

CYCLOTENE* 3000 Series Advanced Electronic Resins

Processing Procedures for CYCLOTENE 3000 Series Dry Etch Resins

1. INTRODUCTION

The CYCLOTENE 3000 series Advanced Electronic Resins derived from B-staged bisbenzocyclobutene (BCB) monomers are dry-etch grades of the CYCLOTENE family of products, and were developed for use as spin-on dielectric materials in microelectronic device fabrication. The CYCLOTENE resins are low dielectric constant and low dielectric loss materials, and feature low moisture absorption, no out-gassing, low temperature cure and excellent planarization (Figure 1). Properties of the CYCLOTENE products are given in Table 1. The CYCLOTENE resins have been widely adopted in a variety of electronic applications, including silicon and compound semiconductor passivation, interlayer dielectric, flat panel displays, IC packaging, integrated passives, MEMS, wafer bonding and 3D integration, and optoelectronic components. There are four formulations of the CYCLOTENE 3000 series products which are commercially available from the Dow Chemical Company, as shown in Table 2.

An additional dry etch product, XUS 35077.00 type 02, was designed for flat panel display applications. Please refer to our processing guide "Technical Processing Guide for Flat Panel Display Applica-tions" for more information on that product.

2. STORAGE

The CYCLOTENE 3000 series resins as well as the ancillary chemicals, including adhesion promoters (AP3000), rinse solvent (T1100), and stripper (Primary Stripper A) are stored at room temperature. The shelf life for CYCLOTENE 3000 series resins at room temperature is two years from the date of manufacture.

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Figure 1. Planarization ratio as a function of metal line width for dry etch grade BCB. The metal line height is 4µm.

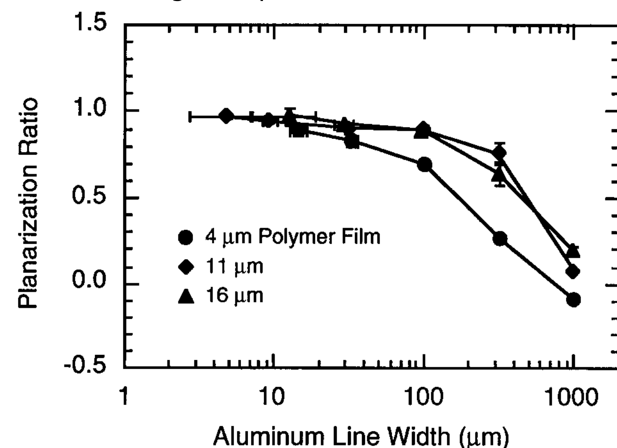


Table 1. Thermal, Electrical and Mechanical Properties of CYCLOTENE 3000 Series Resins

Property	*Measured Value*
Dielectric constant	2.65 at 1-20 GHz
Dissipation Factor	0.0008
Breakdown Voltage	5.3 x 10^{6} V/cm
Leakage Current	6.8 x 10^{-10} A/cm^2 at 1.0 MV/cm^2
Volume Resistivity	1 x 10^{19} Ω-cm
Thermal Conductivity	0.29 W/m°K @24°C
CTE	42 ppm/°C at 25°C
Tensile Strength	87 ± 7 MPa
Tensile Modulus	2.9 ± 0.2 GPa
Elongation	8 ± 2.5 %
Poisson's Ratio	0.34
Residual Stress on Si	28 ± 2 MPa at 25°C
Tg	> 350°C
Moisture Absorption	< 0.2%

Table 2: Formulations of the CYCLOTENE 3000 series products

Solution Properties	3022-35	3022-46	3022-57	3022-63
Solvent	Mesitylene	Mesitylene	Mesitylene	Mesitylene
Viscosity (cSt @ 25°C)	14	52	259	870
Thickness Range❶ (µm)	1.0 – 2.4	2.4 – 5.8	5.7 – 15.6	9.5 – 26.0

❶ The thickness data given above should not be construed as product specification.

3. EQUIPMENT SELECTION

In principle, spin coaters designed for photo-resists and spin-on polymers can be used for the coating of CYCLOTENE resins. However, it is recommended to use a programmable spin coater having the following features: two dispense nozzles (one for adhesion promoter and one for BCB resin), hotplate, backside rinse capability, top side edge-bead removal (EBR), cup rinse, and cup exhaust.

3.1. Pressurized Dispense

In pressurized dispense, either nitrogen or helium can be used. Helium is less soluble than nitrogen in resin solutions under pressure and causes fewer bubbles than nitrogen during dispense and spin coating. Pressure should be released when the resin is not in use.

3.2. Cup Rinse and Exhaust

Cup rinse is recommended at the end of a cassette to prevent the spun-off resin from drying on the cup surface and becoming a source of particles. Cup exhaust should be turned on throughout the entire coating process to evacuate the solvent vapor and to keep mist and polymer fibers below the wafer surface.

3.3. Materials for Delivery System

Teflon is the recommended material for the components of the CYCLOTENE resin delivery system, which include delivery lines, bottles, cap adapters, and filters. Kalrez is recommended for O-rings and elastomeric components. HDPE is not compatible with the mesitylene solvent.

3.4. Waste Dispose

It is recommended to dispose the waste into a container for organic solvents.

4. SPIN-COATING PROCESS

Figure 2 depicts a typical process flow of CYCLOTENE resins on a planar substrate. The detail of the procedure for each of the steps will be described below.

4.1 Surface Preparation

The surface of substrates to be coated with CYCLOTENE resin should be free of inorganic particles, organic residues and other contam-inants. Particles and residues cause coating defects and may lead to subsequent adhesion problems. A brief treatment of O_2 plasma followed by DI water rinse is usually sufficient for general cleaning purposes. If polyimide is present on the substrate, a dehydration bake (e.g., oven or hotplate bake at a temperature of 150°C or higher) followed by oxygen plasma treatment prior to BCB coating is necessary to ensure good adhesion.

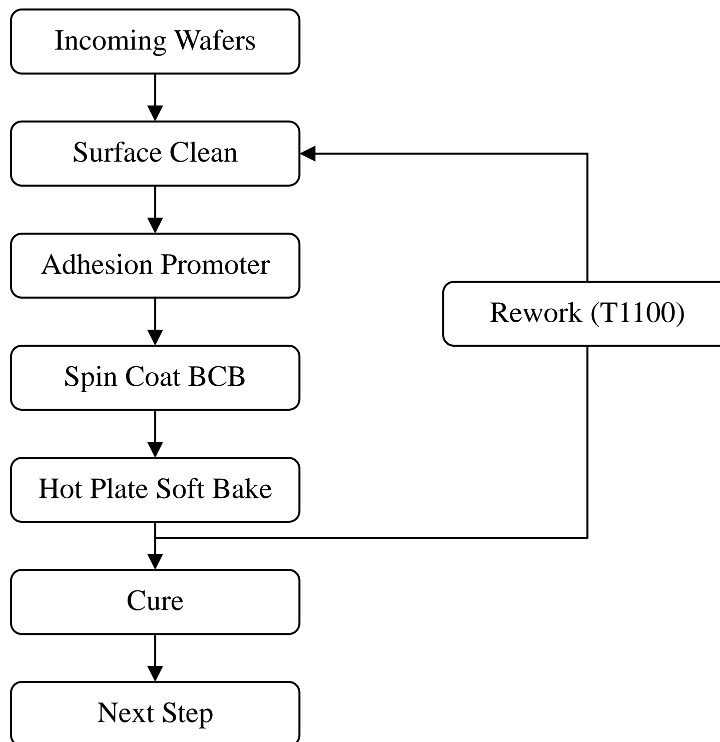
4.2 Adhesion Promoter

Adhesion promoter is always recommended prior to BCB coating. The procedure for apply-ing adhesion promoter on a substrate comprises dispensing, spreading (e.g., 50-300 RPM for 5 seconds), and spin-drying at 3000 RPM for 10-20 seconds. Baking adhesion promoter prior to BCB coating is usually not required, but it can improve the adhesion of BCB to certain substrates. The adhesion promoter available from Dow, AP3000, is effective on most surfaces, including silicon oxide, silicon nitride, silicon oxynitride, aluminum, copper and titanium.

Please refer to our application note "Processing Procedures for BCB Adhesion" for more details on BCB adhesion to other materials.

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

Figure 2: Typical process flow steps for depositing BCB films on a substrate



4.3 Resin Coating

Following the adhesion promoter process, BCB resin is spun onto the substrate. The coating process is comprised of the following steps: dispense; spread; spin coat; backside rinse; topside (EBR); spin dry; and soft bake. The details for each of the steps are described below.

4.3.1 Dispense

Dispense of BCB resin can be done statically or dynamically (rotating the substrate at a speed of 50-200 rpm). For optimal material usage it is helpful to dispense the resin radially from the edge of the wafer to the center, particularly for the higher viscosity formulations. The dispense volume will depend on the size of the substrate and the topography of the substrate surface. Slightly greater dispense volume is often required with increasing topography for a given substrate size.

4.3.2. Spread

Increase the substrate rotation speed to approximately 500 – 750 rpm for 5-7 seconds to spread the resin out from the center of substrate.

4.3.3. Spin Coat

Increase the substrate speed to a rate which is appropriate to achieve the desired coating thickness. Table 3 lists the correlation between cured film thickness and spin speed for each of the CYCLOTENE 3000 series resins. Note that these data are for an open bowl spin coater. When using a covered coater, film thickness will depend on both spin speed and spin time, and will generally be thinner than the values in Table 3.

4.3.4. EBR and Backside Rinse

Adjust the substrate speed to about 500 rpm and dispense the EBR solvent (T1100) for 5-10 seconds to remove the edge-bead (about 1.5

Table 3: Thickness after cure (in microns) versus spin speed.

Spin Speed (RPM)	CYCLOTENE 3022-35	CYCLOTENE 3022-46	CYCLOTENE 3022-57	CYCLOTENE 3022-63
1000	2.26	5.46	13.8	26.2
1500	1.84	4.39	10.7	19.9
2000	1.59	3.76	9.04	16.5
2500	1.43	3.35	7.97	14.4
3000	1.30	3.05	7.21	12.9
3500	1.21	2.82	6.65	11.8
4000	1.13	2.63	6.20	10.9
4500	1.07	2.48	5.84	10.2
5000	1.01	2.35	5.55	9.64

NOTE: The data given above are not to be construed as product specifications.

mm from the edge of the wafer) from the top side of the substrate and to remove any contamination from the backside of the substrate. Top side edge-bead removal not required, but it is recommended. The backside rinse (BSR) should not be omitted.The top side EBR and backside rinse can be performed sequentially or simultaneously.

4.3.5. Spin-Dry

Following the EBR and backside rinse, the substrate is spun at 2000 rpm for 20-30 seconds to dry the backside of the substrate.

4.4. Bake

After the spin coating process, the BCB film should be baked on a hotplate to remove solvents and to "stabilize" the film in order to avoid material flow during subsequent handling and curing. The temperature and time for the bake of the CYCLOTENE resins are not critical. The hotplate temperature can be set from 80°C to 150°C and the time can be as short as 60 seconds.

5. THERMAL CURE

After coating and bake, the films are cured to achieve their final properties. The cure of CYCLOTENE resins can be performed using a variety of tools, including convection oven, vacuum oven, tube furnace, reflow belt oven, and hotplate. Except for early out-gassing of residual solvent, CYCLOTENE resins do not evolve volatiles during cure, thus there are no constraints on the heating rate. (However, note that optimum planarization is achieved with a relatively slow ramp.) The only constraint is that, since films of CYCLOTENE resin are susceptible to oxidation at elevated temperature (≥150°C), the cure must be carried out under an inert atmosphere, with an oxygen concentration below 100 ppm. This condition can be readily achieved by flowing inert gas (nitrogen or argon) through a convection oven, tube furnace, or by using a vacuum furnace or oven.

CYCLOTENE resins can flow during the cure process. For optimum thickness uniformity, the substrates should be cured in a horizontal orientation.

5.1 Soft Cure

The soft or partial cure for the CYCLOTENE family of resins is designed to reach approximately 80% conversion (polymerization) and it is used for successive coating of the resin (i.e., double or triple coats) or multilayer structures (e.g., BCB/metal/BCB) in which the two BCB layers are in contact. See Table 4 for a recommended partial cure profile in a convection oven.

5.2 Hard Cure

The hard or full cure is typically carried out as final cure after all polymer layers of the device structure have been completed, and it is designed to achieve 95-100% conversion. A typical suggested profile for hard cure is 250°C for one hour in a box oven or furnace. See Table 4 for a recommended full cure profile in a convection oven. Cure of CYCLOTENE resins at

Figure 3: The extent of BCB cure as a function of temperature and time.

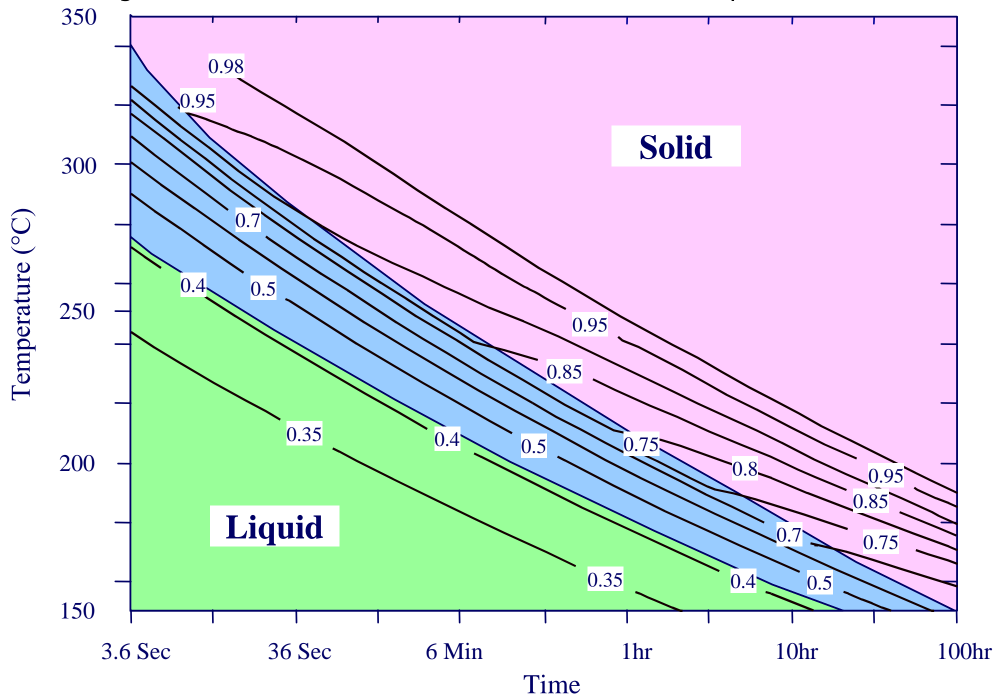


Table 4. Oven cure profiles for Cyclotene 3022.

Step	Partial Cure	Full Cure
1	15 minute ramp to 100°C	15 minute ramp to 100°C
2	15 minute soak at 100°C	15 minute soak at 100°C
3	15 minute ramp to 150°C	15 minute ramp to 150°C
4	15 minute soak at 150°C	15 minute soak at 150°C
5	60 minute ramp to 210°C	60 minute ramp to 250°C
6	40 minute soak at 210°C	60 minute soak at 250°C
7	Cool to <150°C	Cool to <150°C

a temperature higher than 250°C does not adversely affect the properties of the film, but the temperature should not exceed 350°C. Figure 3 presents the extent of cure as a function of cure time and temperature.

6. REWORK

For rework of a BCB film after bake and prior to cure, T1100 is the recommended solvent. This can be done by dispensing T1100 on the track, or by immersing the substrate in a T1100 bath at room temperature. The BCB films after soft cure can be removed by immersing the film in a Primary Stripper A bath at 90-100°C. Removal rate of soft cured BCB film increases with higher bath temperature, and is about 2µm/hour at 90°C and about 6µm/hour at 100°C. After the stripping process with Primary Stripper A, the substrate should be rinsed with isopropanol, followed by DI water rinse and dry. An O_2/CF_4 plasma treatment after strip and rinse will help to completely remove any organic residues. Fully cured CYCLOTENE films are highly resistant to most chemicals, which makes them difficult

to remove. Once the film is fully cured, plasma stripping (oxygen/fluorine plasma) is usually the only viable means of removing it. A piranha (H_2O_2/H_2SO_4) or fuming nitric acid bath will remove fully cured BCB films, but metals and underlying device structures will generally not tolerate such an aggressive cleaning agent.

Please refer to the application note "Rework Procedures for CYCLOTENE 3000 Series and 4000 Series Resins" for more details on rework.

7. PLASMA ETCH

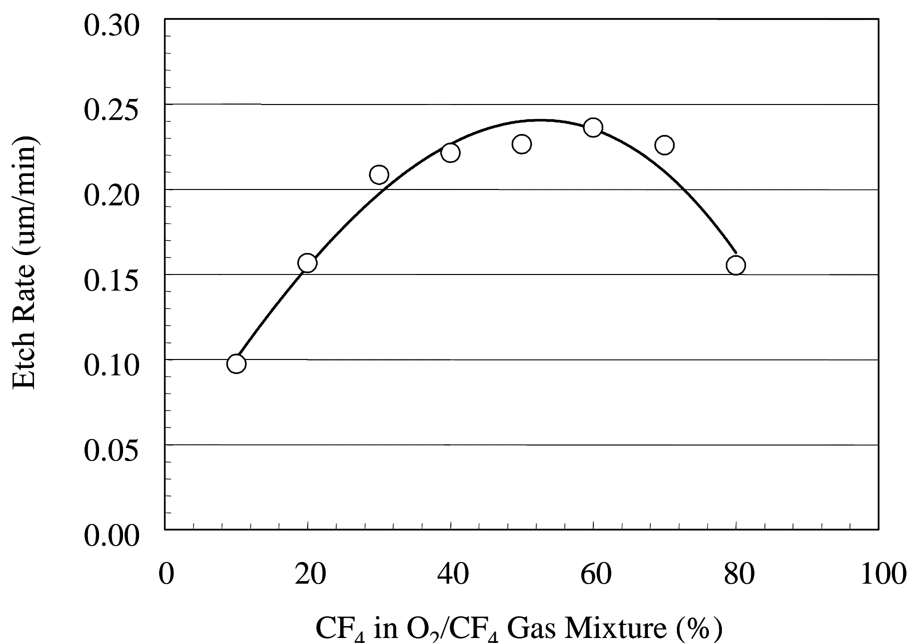
Pattern definition of films made with the CYCLOTENE 3000 resins can be accomplished by means of a plasma etch process in conjunction with photoresist (PR) processing, and using either soft mask or hard mask approaches.

7.1 Etch gases

The plasma used to etch CYCLOTENE films generally requires both oxygen and fluorine species since silicon is present in the backbone of the polymer. A mixture of oxygen and a fluorine-containing gas (CF_4, C_2F_6, C_4F_8, SF_6, NF_3, etc.) has been found to produce a controlled etch rate using parallel plate or reactive ion etchers. Commonly used gas mixtures are 4:1 O_2/CF_4, or 5:1 O_2/SF_6. More fluorine can increase BCB etch rate initially, but when the fluorine component exceeds a certain limit, the BCB etch rate decreases. Figure 4 shows etch rate vs gas composition in O_2/CF_4. SF_6 tends to give faster etch rates than CF_4. Maximum etch rates are achieved with about 55-60% CF_4 in O_2 [1], or about 20% SF_6, or about 20% NF_3 [2]. Though it is generally not recommended, etching of BCB in O_2 without any fluorine has been reported. [3].

An inert gas (N_2 or Ar) can be also added to the reactor to increase the overall pressure in the chamber and moderate the chemical vs. physical components of the plasma. As a result, both etch profile and etch uniformity can be improved. Adding more inert gases can lead to an increased etch rate and higher etch selectivity of CYCLOTENE resins over CVD oxide and nitride. Lower concentrations of fluorine also give better selectivity to nitride. Higher power and pressure can increase BCB etch rates, but may also lead to etch non-uniformity.

Figure 4: Etch rates as a function of gas composition for reactive ion etch process.



Soft cured and hard cured BCB films show similar etch characteristics.

NOTE: Oxygen plasma without a fluorine component can create an undesirable amorphous silicon oxide on the surface, thus, the etching process becomes self-passivating, and the etch rate slows down and eventually stops. The resulting surface SiO_2 layer is brittle and can lead to cracking of the BCB film. In addition, materials deposited on top of this oxide (e.g., metals, CYCLOTENE resins, etc.) typically show poor adhesion. In a via etch scheme the surface of the polymer is protected by the soft mask or hard mask, but the via side walls can be damaged. For these reasons, plasma etching in O_2 is not recommended. Similarly, resist stripping in an O2 plasma should also be avoided.

7.2 Etch tools

A variety of etchers have been used. Both reactive ion etchers (RIE) and inductively coupled plasma (ICP) tools have been used with good results. Downstream etchers have also been used. Barrel etchers are not recommended, because (a) the etch uniformity is quite poor, the etch rate being much greater at the edge than at the center, and (b) the lack of temperature control can lead to film surface oxidation and SiO_2 formation even when fluorine is present.

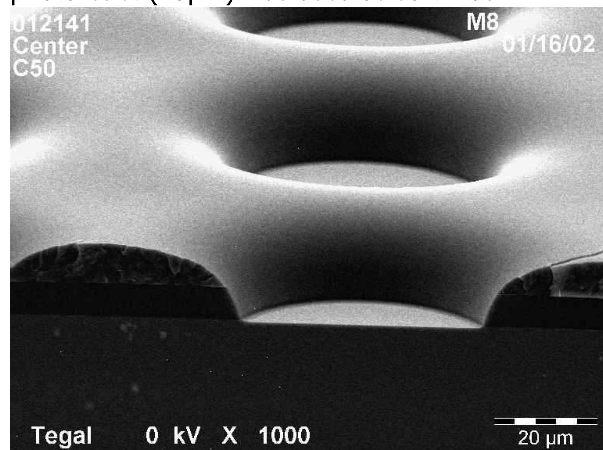
7.3 Soft Mask Process

In this process, the photoresist employed for pattern definition is also used as a sacrificial mask for BCB etching [4,5]. Etch selectivity between BCB and photoresist films is usually found to be about 1:1, so the resist thickness should be greater than the BCB thickness. Compatibility of the resist stripper with BCB should also be considered. Figure 5 shows the etched thick BCB profile using O_2/CF_4 chemistry on Tegal's 981 plasma etcher using a photoresist etch mask, showing sloped side wall profile and no visible etch residues. [6]

7.4. Hard Mask Process

Inorganic materials such as CVD dielectric films (SiO_2, SiN) or metal films (Al, Cr) can be used as a non-sacrificial mask for BCB etching. If an inorganic dielectric material is adopted for the hard mask, the hard mask layer can be retained as a part of the dielectric structure. Due to the presence of fluorine in the etch gas, there will be a finite etch rate of the hard mask material, and its thickness should take this into account. In the case of using a metal as the hard mask, the etchant used for the metal removal should be compatible with BCB. Figure 6 shows etched via profiles in 1µm thick BCB, using a 0.3µm thick oxide hard mask, which was conducted with more complicated etch chemistry on a Lam TCP 9100 etcher. [7]

Figure 5. Field and sidewall view of etched thick BCB (7µm) on Tegal's 981 plasma etcher. AZ-P4620 photoresist (15µm) was used as soft mask.



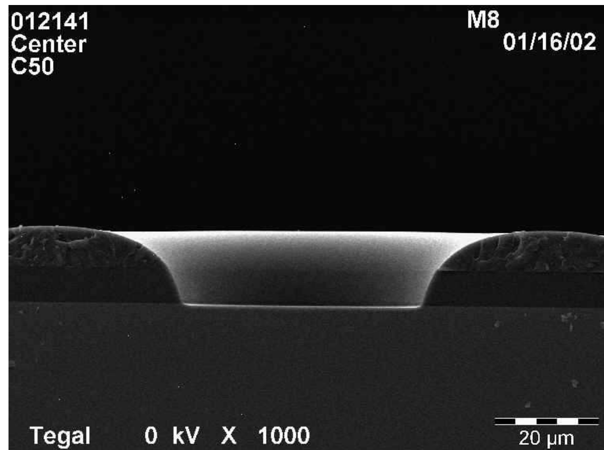
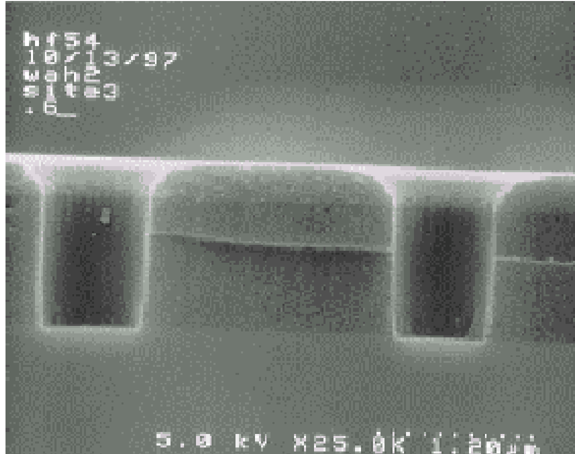


Figure 6. Sub-micron BCB via profile etched in a Lam TCP9100 etcher (Pressure: 10 mTorr, TCP Power: 1500 W, RF Power: 700 W, O_2: 18 sccm, C_2F_6: 2 sccm, N_2: 40 sccm).



8. REFERENCES

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