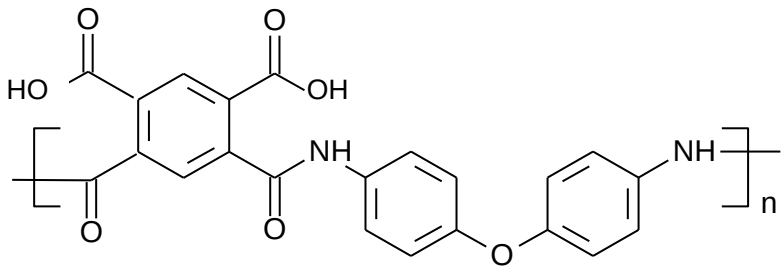
FUJIFILM

Polyamic Acid. Durimide ® 100

The Durimide 100 Series are a range of self priming, non-photosensitive polyamic acid formulations which become fully stable polyimide coatings after thermal curing. They can be photo-imaged using a positive photoresist mask. Softbaked polyimide films are coated with photoresist, softbaked, exposed and post exposure baked. When the photoresist is developed, the polyimide is etched, transferring the pattern from the photoresist into the polyimide. The photoresist is subsequently removed with a solvent rinse and the polyimide thermally cured. The minimum geometry which can be achieved by this method depends upon the thickness of the polyimide at softbake. The smallest resolvable feature is approximately four times the softbake film thickness.

Chemistry and Characteristics

Durimide 100 is a polyamic acid with the following structure:



The Durimide 100 series is available in varying viscosities for producing coatings of varying thicknesses, as indicated below.

Product Characteristics Durimide 100 Series

Parameter		Unit	Range Low	Range High
Kinematic	Durimide 112A	cS	1700	2100
Viscosity (25°C)	Durimide 115A	cS	6200	8300
	Durimide 116	cS	10000	14000
Water Content		%	0	0.5
Sodium		ppb	0	300
Potassium		ppb	0	200
Iron		ppb	0	100
Copper		ppb	0	100

Product Characteristics Durimide 100 Series*

Parameter	Unit	112A	115A	116**
Cured Coating Thickness	μm	1.5-2.5	3-6	4-9
Filtration	μm	0.5	1.0	1.0
Solids Content	% wt	11-12.5	14-15.5	15.2-16.5

*The above are typical values only and are not for specification purposes.
** Durimide 116 does not contain an internal adhesion promoter.

Cured Film Properties Durimide 100 Series

Property	Unit	Typical Value
Tensile Strength at Break	**MPa**	**260**
Young's Modulus	**GPa**	**3.3**
Tensile Elongation at Break	**%**	**80**
Glass Transition Temperature	**°C**	**371**
Thermal Decomposition Temperature	**°C**	**597**
Coefficient of Thermal Expansion	**ppm/°C**	**32**
DCoating Stress (100 silicon)	**MPa**	**20**
Dielectric Constant 1MHz; 0%-50% RH		**3.1-3.4**
Dissipation Factor 1MHz; 0%-50% RH		**0.003-0.009**
Dielectric Strength; room temp. - 50%RH	**V/µm**	**342**
Moisture Absorption @ 50%	**%**	**1.7**
Density	**g/cc**	**1.49**
Refractive Index (Cured)		**1.81**

Adhesion Testing Durimide 100 Series

Tape Pull Adhesion			
Substrate	Boiling Water[1]	Pressure Cooker[2]	
			Time hours
Silicon	5	5	200
Silicon Nitride	5	5	600

[1] ASTM Method D-3359-83: 72 hours boiling water
[2] Test at 2 atm. 120°C

Key Features

Durimide 100 Series polyimide precursors are distinguished by the following characteristics in application and use:

- Self-priming – only “A” versions
- Formulations cover cured film thickness range 2-10 µm
- Patternable using conventional resists and developers
- Excellent adhesion
- High thermal stability
- Improved resistance to stress cracking
- Reduced metal staining
- Reworkable (before final cure)

Process Guidelines

Material Storage and Warm-up

To maintain shelf life, Durimide 100 should be stored in a freezer between –15°C and –30°C. Remove bottle from the freezer and allow to equilibrate to room temperature before opening the bottle. Opening the bottle before complete equilibration can introduce moisture in the material, can lead to difficulties in pumping and can result in large variations in coating performance.

Suggested equilibration times can be found in the following table.

Container Size	Warm up Time at Room Temperature
250g	4 hours
1Kg	12 hours
4Kg	24 hours

Substrate Pre-Treatment

An oxygen plasma treatment and/or dehydration bake at 250°C (oven: 30 minutes, hotplate: 4 minutes; optional) constitute the best preparation process. The choice will depend on individual circumstances.

Durimide polyimides contain an internal adhesion promoter, eliminating the need for an additional priming step. Note also that HMDS (used as a photoresist adhesion promoter) significantly reduces the adhesion of polyimide materials. Use care to ensure that no cross-contamination of either the materials or the coating equipment can occur.

Applying the Polyimide Precursor

Spin Coating

Durimide polyimides are usually spun on in a single coating operation. Spin speed and spin time are adjusted to individual needs depending on the substrate size, shape and mass as well as the desired film thickness and uniformity required. Select spin condition from respective spin curve.

We recommend the following spin procedure. Dynamic dispense 2-5 ml of polyimide onto the center of the wafer. Use a low speed spin of 1000-1500 rpm for 7-25 seconds to spread polyimide to within 5-10 mm of edge of substrate. Then, accelerate to final spin speed and spin for 30-45 seconds. A short sit time of 5-15 seconds after the spread cycle and before the final spin can improve the uniformity in the final film.

Spin Bowl Rinse and Wafer Backside Rinse Options

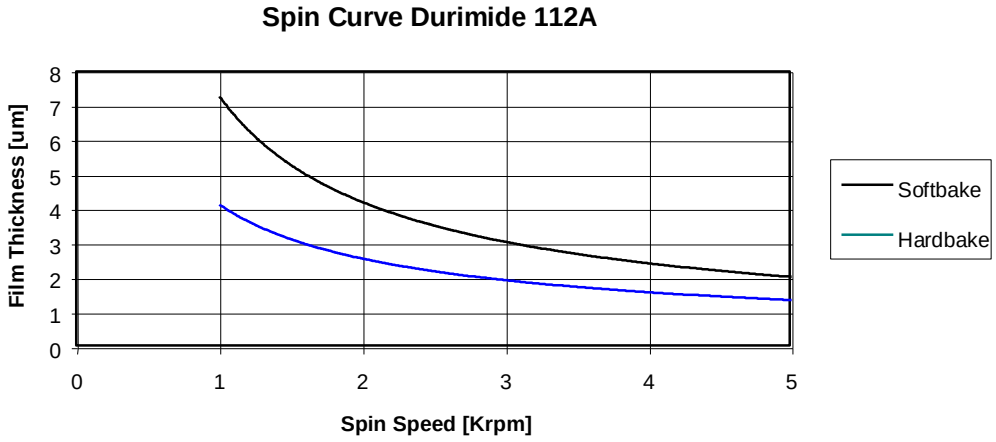
For the ease of keeping the spin bowl clean and free of particles, it is recommended to rinse the spin bowl using the automated spin bowl rinse feature on the wafer track system after each application of polyimide. The recommended solvents are N-methyl-2-pyrrolidone, or cyclopentanone (HTR-D2). Solvents such as gamma-butyrolactone mixtures or cyclopentanone can be used for backside rinse. For edge bead removal, cyclopentanone is the recommended solvent. The spin bowl rinse, the wafer backside rinse and the edge bead removal options are usually available on most wafer track systems. The solvent dispense systems are usually pressurized canisters with 1/8" (I.D.) tubing (Teflon® or similar materials are recommended).

Spin Speed Curves

The following are the spin curves for the Durimide 100 series.

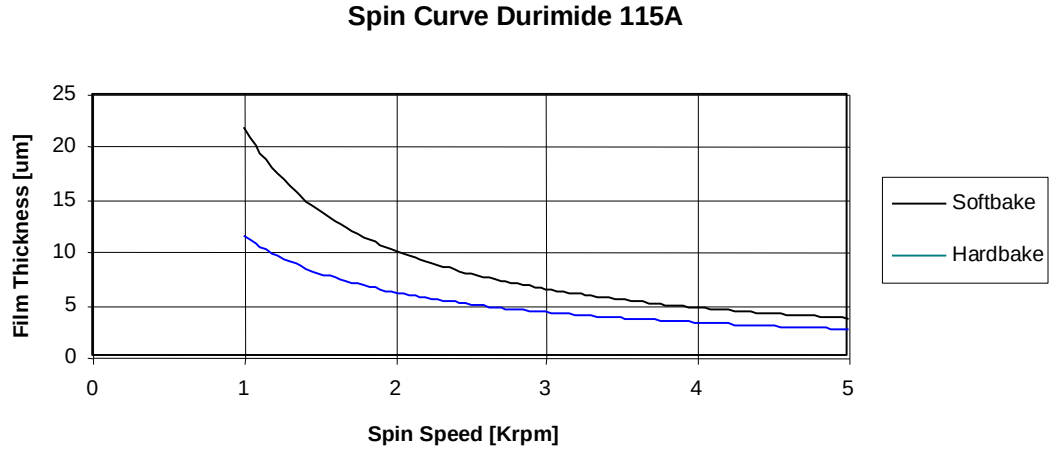
Spin Curve Durimide 112A

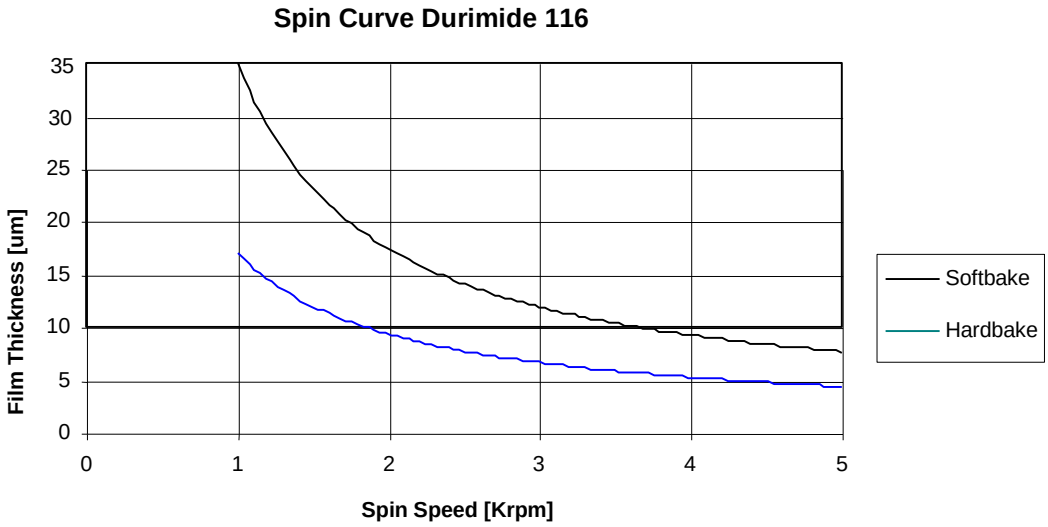
Softbake : 50 sec @ 135°C
Hardbake : 30 min @ 400°C
Spin time : 45 sec
Spread cycle : 700 rpm/4 sec



Spin Curve Durimide 115A

Softbake : 50 sec @ 135°C
Hardbake : 30 min @ 400°C
Spin time : 45 sec
Spread cycle : 700 rpm/4 sec





Softbake

A multiple hot-plate is the easiest arrangement for consistent processing but a convection oven with a nitrogen purge can also be used. Hotplates should have a temperature uniformity of ±1°C to ensure uniform etching. The softbake time on a hot-plate will vary with film thickness but should be between 60 and 300 seconds at a temperature of 120 - 140°C. Higher temperatures and longer times will start the imidization reaction and slow the rate of polyamic acid etch in the developer.

For thicker films (> 10µm softbaked) a two-stage bake is recommended to prevent the formation of coating defects caused by too rapid solvent removal. The first stage should start at 90-110°C for 1-2 minutes followed by a second stage at 130-140°C for 2-5 minutes.

A convection oven alone or in combination with hotplates can also be used. The time in a convection oven will greatly depend on the configuration of the oven, the number of wafers in the oven, etc. Substrates must be oriented horizontally to prevent thickness variations during softbaking.

A combination bake would include a hotplate bake at 90-110°C for 1-2 minutes followed by a convection oven bake at 130-140°C for 30-60 minutes.

Photoresist Coating

The coating process will depend on the type of photoresist used. A coating thickness of 1.5 - 3 µm is suitable depending on the thickness of the polyamic acid coating. The resist must be able to withstand the extended developing time needed to etch the polyimide. Photoresist softbakes range from 1-2 minutes at 110-130°C on a hotplate. The photoresist should be baked at a lower temperature than the polyimide to prevent the formation of an interfacial layer between the two coatings.

Exposure

The exposure dose will be approximately two times that needed for the photoresist alone. Typical exposure energies will lie between 200 and 400 mJ/cm^2.

Post Exposure Bake

A post exposure bake is optional. Post exposure bakes range from 1-2 minutes at 100-120°C. The additional bake hardens the photoresist before the develop and etch process. The post exposure bake should be at a lower temperature than the polyimide softbake.

Development

A TMAH based positive photoresist developer such as OPD 262 or OPD 4262 is recommended. The develop time is dependent on the polyimide softbake, polyimide thickness, exposure dose and develop method. A spray puddle process should include a short dynamic spray time of 6-8 seconds to remove

most of the photoresist and start the puddle formation. An additional 2-5 seconds of spray time is then needed to complete the puddle. Puddle times will range from 20-80 seconds. Rinse 10-20 seconds with DI water at 1000 rpm and spin dry. A high speed water rinse (2-4 Krpm) can aid in removing the dissolved polyimide quickly to prevent redeposition of the polyimide. A double puddle process can be used for thicker polyimide films or processes that require a large percentage of the polyimide to be removed.

An immersion develop process requires times from 20-80 seconds with continuous agitation throughout the cycle followed by a DI water rinse and spin dry.

Photoresist Stripping

The photoresist can be stripped using a variety of common photoresist solvents including FUJIFILM Electronic Materials' RER500, RER550 and RER600 (all of which are also used for photoresist edge bead removal). N-methylpyrrolidone based photoresist strippers should not be used as these will attack and remove the softbaked polyimide as well. Photoresist stripping can be done on a track system. A short 6-10 second spray followed by a spin dry is generally adequate to remove the photoresist. Thicker photoresists may require a second spray process or an additional puddle step to achieve complete removal.

Cure

The final cure can be carried out in a convection or hot-plate oven provided with a nitrogen purge. A typical cure cycle will ramp from room temperature to 400°C at 3 to 6 °C/min. The temperature will be held at 400°C for 30 minutes. To prevent oxidation of the polyimide film, the oven should then be allowed to cool slowly to below 200°C before parts are removed.

Baseline Process

Figure 3 shows a series of typical processes using a Durimide 100 softbake film thickness ranging from 3.6 to 9.5 µm (2.4 to 5 µm cured). These processes together illustrate the range of options available to process Durimide 100 coatings.

Example Processes for Patterning the Durimide 100 Series

		Durimide 100 Material		
Polyimide process step		**112A**	**115A**	**115A**
Coat polyimide		3ml dispense	3ml dispense	3ml dispense
Spin process		dynamic dispense for	dynamic dispense for	dynamic dispense for
		16 seconds @ 600rpm	5 seconds @ 1000rpm	12 seconds @ 1000rpm
		10 seconds @ 0 rpm		15 seconds @ 0 rpm
		45 seconds @ 2100rpm	45 seconds @ 4500 rpm	30 seconds @ 3600rpm
Polyimide softbake		50 seconds @ 135°C	90 seconds @ 130°C	5 minutes @ 130°C
			60 min @140°C convection	
PI softbake thickness		3.6-3.8µm	4-4.2µm	9-9.5µm
Coat photoresist		HPR506	HPR504	HPR506
Photoresist spin speed		1900 rpm	3000 rpm	3500 rpm
Photoresist softbake		60 seconds @ 135°C	90 seconds @ 110°C	60 seconds @ 110°C
Photoresist thickness		3.1µ	1.3µ	2.5µ
Exposure		Canon 501 PLA printer	Canon 501 PLA printer	Canon 1550 M2 stepper
		soft contact mode	soft contact mode	0.43NA g-line
Exposure dose		175mJ/cm2	165mJ/cm2	360mJ/cm2
Post exposure bake		none	2 min @ 140°C	none
Developer		OPD262 or 4262	OPD4262	OPD4262
		immersion develop	spray puddle	spray puddle
		40 seconds	6 sec spray @ 300rpm	6 sec spray @500rpm
		constant agitation	60 sec puddle	60 sec puddle
		DI dump rinser, 4 cycles	30 sec DI rinse @ 300rpm	15 sec DI rinse @ 1000rpm
		rinse/ dryer, 5 minute cycle	15 sec spin dry @ 2000rpm	10 sec spin dry @ 3000rpm
Photoresist strip		10 sec spray acetone	10 second spray acetone	RER500
		10 sec spray isopropanol	6 sec spray isopropanol	5 sec stream @1000rpm
		10 sec spin dry @ 4000rpm	25 sec spin dry @ 2000rpm	10 sec spin dry @ 3500rpm
Cure		2 hour ramp up 25-400°C		
		30 min dwell @ 400°C		
		2 hour ramp down 400-25°C		
Final Thickness		**2.4 µm**	**3.2µm**	**5µm**

Rework

Softbaked Durimide 100 coatings can be reworked using a wet-strip process:

1. NMP at 85 °C for 5 min

2. QZ 3322 Polyimide Stripper at 70 °C for 5 min

3. NMP at Room Temperature for 5 min

4. DI Water Rinse

Fully cured polyimide cannot easily be removed by chemical means. Plasma ashing (O_2 / CF_4 ; 5:1) is the most effective technique.

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