Revised September 2009

PRODUCT BULLETIN

PI-2600 Series – Low Stress Applications

PI-2600 Series products provide high molecular weight, polyimide precursors based on BPDA/PPD (biphenyldianhydride/1,4 phenylenediamine) backbone chemistry. The rigid rod polyimide structure of cured PI-2600 products exhibits a desirable combination of film properties such as low stress, low CTE, low moisture uptake, high modulus and good ductility for microelectronic applications.

Product Description

PI-2600 Series products are supplied as polyamic acid precursors dissolved in an n-methyl-2-pyrrolidone (NMP) based solvent carrier suitable for spin coating applications (solution properties are shown in Table 1). These solutions can be coated and patterned over a variety of substrates and metal surfaces such as silicon, alumina, silicon nitride, polyimide, patterned aluminum or chrome/copper. After application, the polyamic acid precursor is thermally cured into a fully aromatic polyimide film.

The cured film properties of these materials are ideally suited as a dielectric layer for most semiconductor and MCM-D applications or wherever thick films or stacked layers of metallization are required. Patterning is typically done by dry etch or laser ablation techniques.

The properties of PI-2600 series cured films are compared in Table 2 to the properties of other cured polyimides. When fully cured, PI-2600 series are not attacked by most solvents commonly found in a semiconductor fab, including:

- Acetone
- Cresols
- Alcohols
- n-methyl-2-pyrrolidone
- n-butyl acetate
- Aliphatic Hydrocarbons

Fully cured PI2610-Series polyimides can be attacked by strong bases and acids, including: NaOH, KOH, hydrazine, fuming nitric acid, concentrated sulfuric acid, and molten salts.

Processing Details

Apply Adhesion Promoter

An aminosilane based adhesion promoter such as VM-651 or VM-652 should be used to enhance adhesion to silicon, ceramic or patterned metallization. Prior to application the substrate should be free of particles and any surface contamination. The maximum recommended hold-time between application of adhesion promoter and polyimide apply is 48 hours.

Apply Polyimide Precursor

PI-2600 series solutions are highly viscous due to their high molecular weight. Application can be accomplished by manual dispense such as an automatic syringe for prototyping or by a dispensing pump or comparable system on automated lines capable of handling high viscosity, NMP based, solutions. Never open a refrigerated bottle of polyimide precursor until it has had time to fully warm up to ambient temperature.

General guidelines for dispensing materials of this type:

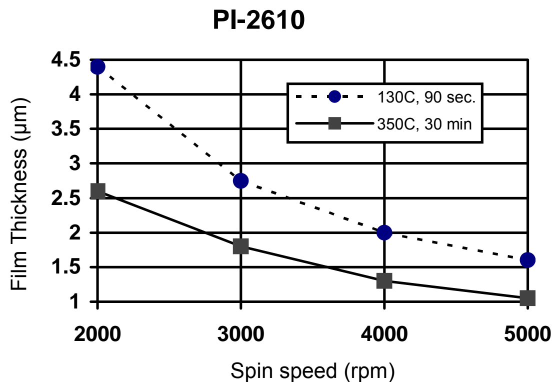
- For best results, coating should be done in a clean room environment, with the relative humidity level less than 50%.
- Always coat substrates which are at room temperature.
- Dispensing should be done in the center and as close to the substrate as possible.
- Never trap air into the solution.
- Take time to allow any bubbles to dissipate out of solution; if left in, comet-like coating defects could result.
- A clean-off at dispense is necessary before the spinning.
- Allow a short delay prior to spin for the polyimide to flow as far as possible and relax.

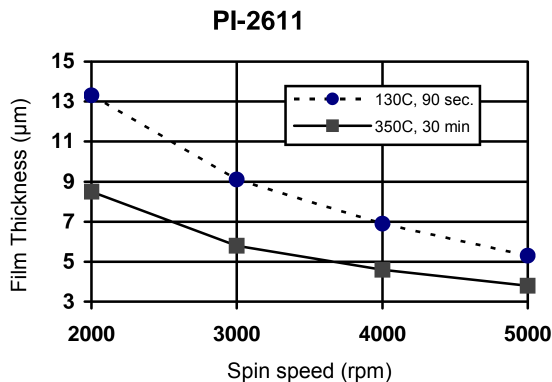
Both static and dynamic dispensing techniques may be used depending on substrate size and available tooling. Typically, static dispense is the easiest to integrate but requires more material per substrate. Dynamic dispense uses less material, but requires greater control during operation. In either case, it is important to assure that the solution is dispensed in the exact center of the wafer. Acceleration to final spin speed should be as slow as possible to allow the coating to flow across the substrate. Often one or more intermediate spin speeds can be used to allow the solution to gradually cover more than 80% of the substrate before continuing on to the final spin speed.

The final spin speed and spin time is determined by the film thickness required (see charts below). To reduce backside contamination potential it is often beneficial to prolong the spin cycle until the bulk of the excess solution has been removed from the substrate. Longer spin times will improve coating uniformity but will reduce the film thickness. In production applications an edge bead remover (EBR) and/or backside rinse (BSR) maybe added to the coating cycle to remove coating from the edge and back of the wafer prior to baking. Commercially available NMP or cyclopentanone based solvent blends can be used for this purpose.

Spin Speed Curves

(Coated for 30 seconds at indicated speed)





Soft Bake

A soft-bake is typically done after coating on in-line hot plate(s) on the coater track. Soft-bake temperatures range from 130 – 200°C for 90 – 180 seconds in the full contact or proximity mode. Detached hot plates or convection ovens can also be use for the soft-bake. After spinning and during soft-bake the wafers should be kept in a horizontal position. Only ventilated ovens should be used for baking. Soft-bake times in convection ovens are typically 30 – 40 minutes.

Thick films of polyimide precursor can be obtained through multiple coating techniques. An intermediate soft-bake is typically performed between coats at 170°C on a hot plate(s) or in a convection oven. It is possible to spin apply 2 – 4 coats in this manner prior to final cure.

Curing

The PI-2600 Series curing process converts the polyamic acid precursor into a fully aromatic, insoluble polyimide film and drives off the NMP solvent carrier. This process requires elevated temperatures and controlled environments to achieve the best results. There is sufficient energy at 200°C to nearly complete the polyimide imidization process. However, higher temperatures are required to completely dissociate the carrier solvent, fully imidize the film and complete polymer orientation, thereby optimizing electrical and mechanical properties.

Final curing can be done in a programmable oven or diffusion tube furnace. An inert atmosphere such as nitrogen or forming gas is preferable although air can used as the ambient up to 300°C. The loading temperature can be at ambient or at the previous soft-bake temperature. Ramp rates are predicated around film thickness and substrate composition. Nominally 2 – 4°C/minute can be used as a starting point.

Final cure temperatures are predicated around the desired ultimate cured film properties and subsequent processing temperatures. Nominally 350°C for 30 minutes is an adequate cure for most applications.

Patterning

Both dry etch processing and laser ablation techniques have become the preferred process routes for patterning PI-2600 Series solutions. These films are difficult to pattern using traditional wet etch techniques due to the molecular structure and inherent film density.

For dry etch processing, a non-erodible dry etch mask is deposited over the cured film. This etch mask should have an inherently lower etch rate than the polyimide in an oxygen based, dry etch gas mixture. Patterned aluminum and CVD have been successfully used as dry etch masks.

Specific dry etch conditions depend on the etch tool (plasma or RIE), film thickness and resolution. An etch gas composition of 75– 80% oxygen and 15– 20% CF_4 is typical. Power density is usually 200 – 500 watts and vacuum pressure in the range of 100 – 500 mTorr. Vias can be tapered by reducing the vacuum pressure to less than 100 mTorr at the end of the etch process.

After dry etching it may be necessary to clean patterned vias of residuals. Reverse sputtering or a low pressure oxygen plasma clean may be used for this process. This process will slightly roughen the surface of the film, which is desirable to enhance the adhesion of metals or the re-coating of subsequent polyimide layers.

Metallization and Multiple Layers

The high modulus, low stress and thermal stability of cured PI-2600 Series films make them well suited for most thin film metallization processes. Building multiple layer circuits is a straight forward process. Prior to deposition it is helpful to slightly roughen the surface of the cured polyimide film using oxygen plasma to improve the mechanical adhesion of the next metallization or polymeric layer. A dehydration bake performed between 100 – 200°C is also recommended prior to metal deposition but not necessary for subsequent polyimide layers. This step can be done in the deposition tool. Convection ovens (30 -60 minutes) or hot plates (2 – 3 minutes) may also be used for this step.

Adhesion promoters such as VM-651 or VM-652 are frequently used in the application of polyimide precursors over patterned metallization. This process is essentially the same as the one detailed above.

This processing outline has been printed as a guideline. Actual production processes are fine tuned around the circuit construction (or materials stack) and the integrated processing tools. For further details on PI-2600 Series processing consult your HD MicroSystems Technical Service Representative.

Storage/Shelf Life

PI-2600 Series products are stable at cleanroom temperatures (21°C) for about four weeks with no significant change in properties. When stored at -18°C, shelf-life is two years from date of manufacture. Moisture contamination is detrimental to stability and must be avoided. Containers should be brought to room temperature before opening to avoid moisture condensation inside the bottle.

Example of Typical Process Conditions

Application of Adhesion Promoter

(VM-652 or diluted VM-651)

- Dispense on static substrate, 3 seconds
- Hold for 20 seconds
- Spin Dry for 30 Seconds

Apply Polyimide Precursor

- Dispense on static substrate
- Spread at 500rpm for 5 seconds
- Spin at final speed for 30 seconds
- EBR / Backside rinse, 10 seconds
- Spin Dry, 15 seconds
- Hot plate bake at 90°C for 90 seconds, followed by 150°C for 90 seconds. (optionally repeat for thicker layers)

Cure Polyimide

- Heat from RT to 350°C, ramp rate 4°C/min
- Hold at 350°C for 30 minutes
- Gradual cooling to RT

Pattern Polyimide

Dry Etch Process

- Dehydration bake: 100-200°C, 30 minutes
- Deposit dry etch mask
- Apply photoresist over etch mask
- Image desired pattern
- Load wafers in dry etch tool
- Set parameters to pattern etch mask
- Reset parameters to pattern polyimide
- Reset parameters to strip dry etch mask
- If necessary, clean vias using back sputtering or low pressure plasma

Table 1. Solution Properties of PI-2610 and PI-2611

Test	Units	PI-2610	PI-2611
Solids	%	10.5 ± 1	13.5 ± 1
Viscosity	Poise	25–30	110–135
Chloride Content	Maximum ppm	5	5
Sodium or Iron Content Potassium or Copper Content	Maximum ppm	1.0 0.5	1.0 0.5
Total Metals	Maximum ppm	10	10
Ash	Maximum %	0.10	0.10
Density	g/cm^3	1.064 ± 0.013	1.082 ± 0.012

Table 2. Comparison of PI-2611 Cured Film Properties with Other Polyimides

	Units	PI-2611	PI-5878G	PI-2525
Tensile Strength	MPa	350	260	130
Elongation	%	100	120	90
Density	g/cm	1.40	1.42	1.39
Modulus	GPa	8.5	2.3	2.5
Moisture Uptake	%	0.5	2 - 3	2 - 3
Stress (10 µm film)	MPa	2	16	37
Glass Transition Temperature	°C	360	400	325
Melting Point	°C	None	None	None
Decomposition Temperature	°C	620	580	550
Weight Loss (500°C in air, 2 hr)	%	1.0	3.6	2.9
Coefficient of Thermal Expansion	ppm/°C	3	20	40
Coefficient of Thermal Conductivity	cal/cm·sec °C	25×10^{-5}	37×10^{-5}	35×10^{-5}
Specific Heat	cal/g/°C	—	0.26	0.26
Dielectric Constant (at 1 kHz, 50% RH)		2.9	3.5	3.3
Dissipation Factor (at 1 kHz)		0.002	0.002	0.002
Dielectric Breakdown Field	V/cm	$>2 \times 10^6$	$>2 \times 10^6$	$>2 \times 10^6$
Volume Resistivity	Ω·cm	$>10^{16}$	$>10^{16}$	$>10^{16}$
Surface Resistivity	Ω	$>10^{15}$	$>10^{15}$	$>10^{15}$

United States

HD MicroSystems
250 Cheesequake Road
Parlin, NJ 08859-1241
800-346-5656 ext. 13, 14 (Phone)
732-613-2502 (Fax)

10080 North Wolfe Road, SW3-200
Cupertino, CA 95014
800-346-5656 ext. 11 (Phone)
408-996-0508 (Fax)

Japan

HD MicroSystems, Ltd.
Nikkyohan Building 3F
4-25 Koraku 1-Chome, Bunkyo-ku
Tokyo 112-0004, Japan
81-3-3868-8124 (Phone)
81-3-3868-8126 (Fax)

Europe

HD MicroSystems GmbH
Hugenottenallee 173-175
63263 Neu-Isenburg
Germany
49-6102-18-1823 (Phone)
49-6102-18-1824 (Fax)

Internet
www.hdmicrosystems.com

HD MicroSystems liability is expressly limited by HD MicroSystems' Conditions of Sale shown on Seller's price list or Buyer's copy of Seller's order acknowledgement form (if used) and Seller's invoice. All technical advice, recommendations and services are rendered by the Seller free of charge. While based on data believed to be reliable, they are intended for use by skilled persons at their own risk. Seller assumes no responsibility to Buyer for events resulting or damages incurred from their use. They are not to be taken as a license to operate under or intended to suggest infringement of any existing patent.
Caution: Do not use in medical applications involving permanent implantation in the human body.