HD MicroSystems™
An Enterprise of Hitachi Chemical and DuPont Electronics

Revised September 2009

PRODUCT BULLETIN

PI-2545
Wet Etch Applications

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1. Introduction

HD MicroSystems' PI-2545 is an established, high temperature coating which has been used for a variety of microelectronics applications. The product has a long, established track record in microelectronics and has been used as a thin film dielectric and overcoat layer in semiconductor fabrication and in advanced packaging. Application is by spin coating. Patterning is typically done in conjunction with positive photoresist, using a "wet etch" process on standard coater tracks. Cured films of PI-2545 are very ductile and have a glass transition temperature [Tg] in excess of 400°C. A primary application area for PI-2545 is as an interlayer dielectric stress and secondary passivation layer in the fabrication of semiconductors or other thin film circuits.

2. Product Description

PI-2545 is formulated as a high molecular weight, polyamic acid precursor in an NMP [N-methyl-2-pyrrolidone] based solvent system. After being applied to a substrate such as a silicon wafer, the precursor is thermally converted into an intractable polyimide film. The inherent thermal stability and low modulus of PI-2545 make it well suited for use in high temperature applications involving thin film metalization and high temperature solders.

Very high purity monomers are used in the synthesis of PI-2545 to achieve very low ionic content, high coating quality required for all microelectronic applications. The spin coating thickness of PI-2545 ranges from 1.5 to 3 microns when fully cured at a spin speed range of between 5000 to 2000 rpms. PI-2545 should be used with VM-651 or VM-652 adhesion promoter in most applications to assure good adhesion to the underlying surface or substrate.

A wet etch processing is frequently used to pattern PI-2545, although both dry etch and laser ablation patterning techniques have also been successfully implemented. Excellent process latitude in wet etch processing can be achieved with PI-2545 due to its composition and tight manufacturing specifications. The product is stable at room temperature and has very long shelf life if stored frozen (-18°C). Packaging is typically in HDPE [high density polyethylene] clean room bottles.

3. Key Features:

- High Tg, thermally stable at temperatures approaching 500°C.
- Patterns with positive resists and standard aqueous developers
- Tapered via profiles
- Cured films are ductile and have a low CTE
- Wide wet-etch process latitude
- Good room temperature (RT) viscosity stability
- Resistant to common wet and dry processing chemicals

4. Availability and Storage

PI-2545 is available in one liter and one gallon container sizes. Nowpak and smaller containers sizes can be special ordered. The product is shipped cold and should be stored at a temperature of –18°C (freezer temperature) upon receipt. The product has a shelf life of one or more years from date of receipt when kept under cold storage. Room temperature [RT] stability is 2 weeks. Stored solutions should be allowed to warm up to room temperature before opening to avoid moisture condensation on the inside of the bottle. To avoid solvent loss, bottles should be kept tightly sealed when not in use.

5. Safety and Handling

During handling of PI-2545 adequate ventilation should be provided. Direct skin and eye contact should be avoided. Exposed areas should be flushed with water immediately. Solvent-resistant gloves, goggles and safety masks should be utilized. Consult the PI-2545 Material Safety Data Sheet (MSDS) for additional toxicity/health hazards information.

6. Wet Etch Processing

Basic Process

Prior to cure PI-2545 is a high molecular weight polyamic acid precursor. This precursor is reactive with mild bases such as positive photo resist developer.

In a typical wet etch semiconductor process, the substrate is primed with VM-651 adhesion promoter, followed by PI-2545 apply. After application the coating is given a soft bake to remove the solvent carrier and partially imidize the film. Positive photo resist is applied over the polyimide precursor and imaged to define the desired pattern in the underlying film. The positive photo resist is then developed. During development, the developer will define a pattern in the photoresist. Being a mild base, the developer will then also wet etch the un-masked underlying layer of polyamic acid precursor. After develop and rinse the photoresist is removed using a commercial stripper. The patterned polyimide precursor is then cured in an oven or furnace into a fully aromatic polyimide film. A plasma de-scum is frequently used to remove any remaining surface residues in the open patterned areas.

The soft bake step is one of the most critical process parameters along with overall process consistency. Good quality coating and developer tracks will make the process more robust and enhance yields.

The processing of PI-2545 should be performed in standard clean room conditions. Yellow light should be used in areas where the photo resist is processed. Clean room temperature and relative humidity conditions should be controlled for consistency (± 2.0°C, ± 2% RH) to obtain the best processing results.

6.1 Substrate Preparation

Substrates should be clean and dry prior to use. Oxygen plasma cleaning followed by a wet cleanup with an organic stripper solution (Tokyo Ohka S-l06) to remove trace organic contaminants is recommended. (Trace organic contaminants can degrade adhesion to the substrate during processing or after curing.)

6.2 Surface Priming

Prior to PI-2545 application, the substrate should be primed with an adhesion promoter such as VM-651 or VM-652. The adhesion promoter is applied to the wafer and spun at a high rpm for about 60 seconds and then given a 60 second hot plate bake. VM-651/652 will greatly enhance the adhesion of PI-2545 to silicon, oxides and most metals. The adhesion promoter is activated during the soft-bake process cycle. The VM-651 product is sold as a concentrate. This adhesion promoter is typically mixed as a 0.1% solution in deionized water and discarded after a 24hour period.

6.3 Spin Coating

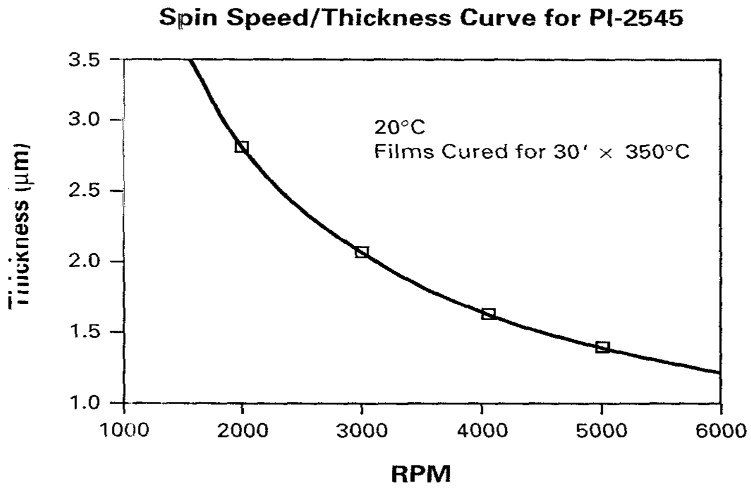
PI-2545 can be coated onto silicon, a variety of metalizations, oxides or other semiconductor and ceramic substrates. An adhesion promoter, should be applied to the substrate prior to polyimide apply. The polyimide precursor solution is viscous. There are some guiding principles for dispensing materials of this type. The substrate and coating solution should both be at room temperature. Never trap air into the solution. This can occur when changing bottles or within the dispense lines. All bubbles take time to dissipate out of solution. If left in, coating defects or “comets“ will result. Dispensing should be in the center and as close to the substrate as possible. A clean cut-off at dispense is necessary before the spin process starts. It may be necessary to implement a short delay prior to spin to allow the polyimide to flow as far as possible and relax.

The volume of the dispensed should remain constant for each wafer to ensure good wafer-to-wafer uniformity. Low spin speed and/or short spin times can impact film uniformity. Both static or dynamic dispense may be used. Static dispense is the easiest, but requires more material to be dispensed for each substrate. Dynamic dispense uses less material, but requires greater control during dispense to ensure that the polyimide strikes the exact center of the substrate. Any deviation can result in poor coating quality.

The acceleration to final speed should be as low as possible to allow gradual flow of the solution across the substrate. Often one or more intermediate spin speeds are used to allow the polyimide to gradually cover more than 80% of the substrate before continuing on to the final speed. To reduce backside contamination, it is often beneficial to prolong the spread cycle until the bulk of the excess polyimide has been removed from the substrate. The final spin speed and time is determined by the film thickness required. Longer spin times will improve coating uniformity, but will also reduce the film thickness. The standard deviation for a soft baked film on an 8 inch wafer can be as low as 0.2 microns. The actual coating thickness obtained for a given set of spin coating conditions will depend on a number of parameters such as equipment type, wafer size, surface topography, ambient conditions and soft bake conditions

In semiconductor applications, an edge bead removal (EBR) and backside rinse process may be added to the coating cycle to remove polyimide precursor from the edge and back of the wafer prior to baking. NMP (N-methyl-2-pyrrolidone) or NMP/IPA (isopropanol) can be used for this purpose along with other commercial preparations optimized for semiconductor processing.

6.4 Spin Speed Curve



Cure Conditions: 30 minutes, 200°C; 30 minutes, 350°C

6.5 Soft Bake

After application of the polyimide precursor, a soft bake process is required. The primary objectives are to 1) drive off carrier solvents from the coating and produce a tack-free surface for resist coating, and 2) to provide sufficient resiliency so that the coating will not delaminate during the wet etch patterning or be attacked or by liquid photo resist strippers. Coated substrates can be soft baked on one or more hot plates or in a vented convection oven. The substrates must remain in a horizontal (level) position during the soft bake process since the coating is still liquid after spin application and not prone to air drying.

Coated substrates should be cooled to ambient temperature prior to the application of photo resist. A chill plate is recommended for cooling after soft bake when using linked process tools. Once soft baked, the coated substrates can be stored for up to 24 hours in a wafer cassette box under clean room conditions prior to resist apply.

6.6 Choice of Photoresist

Polyimide precursors of this type can be patterned using common positive photoresist. The underlying film can act as is an anti-reflective layer as there is significant absorption between 350 and 450 nm. This absorption can significantly reduce substrate reflection effects on the photoresist, usually seen as “notching“ after development.

The photoresist should be selected with the correct wavelength to suit the exposure tool in use. As a general guide, formulations with good adhesion in wet etch semiconductor applications perform well. Other attributes include:

- Compatibility to standard alkaline positive photoresist developers
- Low contrast performance so that a soft sidewall profile is always produced
- Capability to produce cleanly developed via holes in thick resist coatings
- Good development latitude, especially when over-developed
- The ease of producing a minimum dried 1-2 µm film thickness

- After soft bake the polyimide precursor coating has minimum solubility in typical photoresist solvents. Photoresist can therefore be coated directly onto the polyimide precursor coating without inter-layer mixing. The PI-2545 is compatible with a wide range of PGMEA and ethyl lactate based positive tone resists

6.7 Photo Resist Application
Substrates should be coated directly with the resist selected. No dehydration bake should be used as this could make the polyimide totally insoluble in the developer. An HMDS vapor prime is not necessary. Resist thickness can be a critical wet etch process parameter and can be optimized to achieve the best wet etch resolution. A nominal resist thickness of 1.0 to 1.5 microns is recommended as a starting point. Once coated, the resist should be given a soft bake at 90°C either in a convection oven for 30 minutes or on a hotplate for 60 seconds. Once coated and baked, coatings may be held up to 24 hours before exposure.

6.8 Photo Resist Exposure
Typical exposure: 50 to 150 mJ
Once exposed, development should take place within 8 hours.

6.9 Photoresist Development / Polyimide Precursor Etch
A single step is used to develop the photoresist and etch the underlying polyimide precursor layer. Most alkaline positive resist developers will dissolve both exposed photoresist and polyimide precursor at varying rates. The choice of developer can impact the quality of the image after development. Best results have been obtained using a developer with a normality of 0.26 [0.26N].

Polyimide precursor layers up to 5 microns can usually be developed quickly and cleanly with developer that is at ambient temperature. Both spin spray and puddle development techniques may be used. After development of the resist, a water rinse should be used to remove the developer. The substrate can then be spun dry.

When thicker polyimide precursor layers need to be processed, it is often beneficial to heat the developer to between 23°C and 25°C. This accelerates the dissolution of the polyimide precursor while having minimal effect on the solubility of the photoresist. In more extreme situations, this may be coupled with a double puddle process. The second puddle is used to develop only the polyimide precursor layer.

Once developed, wafers may be held up to 8 hours before stripping the resist.

6.10 Resolution
The aspect ratio for wet etched polyimides precursor is about 1 to 5. Finer resolution can be achieved but is predicated on factors such as film thickness, feature shape and processing tools and general process conditions.

6.11 Resist Strip
After developing, the photoresist should be stripped off before curing. This step is usually carried out on automated track equipment to reduce surface contamination with resist residue. Resist solvent strippers such as PGMEA or N butyl acetate can be used along with a variety of commercial strippers or cleaners.

6.12 Cure Process

The cure heating cycle drives out the remaining carrier solvent and converts the polyimide precursor (or polyamic acid) into an insoluble polyimide film. This process requires elevated temperatures and controlled environments to achieve the best results. As the process continues, water is released as a by-product of the imidization reaction. There is sufficient thermal energy at 200°C to complete about 90% of the imidization, but higher temperatures are required to completely drive off the carrier solvents and complete the imidization process, thereby achieving optimum mechanical and dielectric properties. Final curing is usually done between 300-375°C, although both lower and higher cure temperatures have been used in production applications. A typical cure schedule is detailed in the Processing Outline below.

The final cure should be carried out in an inert atmosphere. Nitrogen or forming gas may be used. A programmable high temperature oven or furnace is the recommended curing tool with a flow rate of about 10 liters per minute for best results. Air may be used for the curing atmosphere up to 200°C. Above this temperature, an inert atmosphere should be used. Curing ramp rates (up and down) can impact the stress level in cured films. Generally, lower ramp rates result in lower stress, however stress level is usually not an area of concern for most PI-2545 applications. After cure, patterned films are frequently given a mild plasma de-scum to remove and organic residues

6.13 Process Modifications

Numerous process modifications with wet-etch polyimides have been reported in the literature to improve resolution, side-wall profiles or mechanical properties. Some examples involve IPA [isopropanol] rinses, polyimide re-etch sequences and/or modified pre-bake or cure schedules. Some of these modifications have not been fully tested or characterized by HD MicroSystems. For further information contact your HD MicroSystems Technical Representative.

7. General Processing Outline PI-2545

Application of Adhesion Promoter

- Dispense VM-651 or VM-652 on static substrate, 3 seconds
- Hold for 20 seconds
- Spin dry for 30 seconds

Bake Adhesion Promoter (optional)

- On hotplate at 120°C for 60 seconds

Polyimide Precursor Coating

- Dispense on static substrate
- Rotate at 500 rpm for 5 seconds
- Spin at desired spin speed for 30-60 seconds (see spin speed curve)
- EBR/Backside rinse, 10 seconds
- Spin dry, 15 seconds

Soft Bake

- On one or more hot plates at 140°C in proximity for 2 to 6 minutes

Coat Photoresist

- Dispense, 3 seconds
- Spread at 500 rpm for 5 seconds
- Spin at final speed for 30 seconds
- EBR / Backside rinse for 5 seconds
- Spin dry for 15 seconds

Soft Bake Photoresist

- On hot plate at 90°C for 60 seconds

Exposure

- 50 mJ to 150 mJ

Development

- Developer: TMAH 0.26N at 21°C
- Rinse: DI water

Puddle Development process:

- Dispense (100 rpm) 5 seconds
- Puddle 20 seconds
- Dispense (100 rpm) 5 seconds
- Puddle 40 seconds
- Rinse (1000 rpm) 15 seconds
- Spin dry (5000 rpm) 15 seconds

Resist Strip

PGMEA, N-Butlyacetate or standard resist stripper

- Dispense (100 rpm), 5 seconds
- Puddle, 15 seconds
- Dispense (100 rpm), 5 seconds
- Puddle, 15 seconds
- Spin dry (5000 rpm), 15 seconds

Cure

Curing should be done in a furnace or oven using the following cure profile:

- Load wafer cassettes
- Heat from room temperature to 200°C, ramp rate: 4°C/minute in air or nitrogen
- Hold time at 200°C for 30 minutes in air or nitrogen
- Heating from 200°C to 350°C, ramp rate: 2-5°C/minute in nitrogen
- Hold time at 350°C for 60 minutes in nitrogen
- Cool down to <90°C, ramp rate: <5°C/minute

8. Solution Properties

	PI-2545
Solids content (%)	14.0 +/-1.0
Viscosity (Poise)	11.0 +/- 2
Solvent (NMP/Aromatic Hydrocarbon)	80% / 20%
Water	0.5% max.
Chloride content	5.0 ppm max.
Sodium content	1.0 ppm max.
Copper content	0.5 ppm max.
Iron content	0.5 ppm max.
Potassium content	0.5 ppm max.
Total metals	10.0 ppm max.

9. Cured Film Properties (400°C Final Cure)

▪ Tensile strength (MPa)	260
▪ Elongation (%)	100
▪ Modulus (GPa)	2.3
▪ Stress for 10µm film thickness(MPa)	18
▪ Moisture uptake at 35% Humidity (%)	1.2
▪ Moisture uptake at 85% Humidity (%)	3.1
▪ Dielectric constant in X,Y plane (at 1 kHz, 50% RH)	3.5
▪ Dielectric constant in Z plane (at 1kHz, 50% RH)	3.3
▪ Dissipation factor	0.002
▪ Dielectric breakdown field (volts/cm)	> 2×10^6
▪ Coefficient of thermal expansion,1µm film (ppm)	13
▪ Glass transition temperature	> 400°C
▪ Decomposition temperature	580°C
▪ Weight loss (% at 500°C, 60 min)	1.86
▪ Refractive index	1.78

10. Rework & Solvent Resistance

Prior to cure, PI-2545 is soluble in NMP (N-methyl –2-Pyrrolidone), DMAC (dimethyl acetamide), GBL (gamma-butyrolactone) DMSO (diethyl sulfoxide) and DMF (dimethyl foramide), Before curing, PI-2545 can be stripped for rework with one of a number of different commercial cleaners recommended for polyimide precursor removal. Oxygen plasma can be used to remove both uncured precursor and cured polyimide.

When fully cured, PI-2545 exhibits excellent resistance to most non-oxidizing acids at room temperature and is not attacked by solvents such as:

- Acetone
- Cresols
- Alcohols
- Toluene
- Aliphatic hydrocarbons

The cured films can be stripped by 49% HF solution and will also be attacked by strong acids and bases including such as hot NaOH or KOH, hydrazine, fuming nitric acid, sulfuric acid and molten salts.

11. Summary

PI-2545 is high molecular weight polyimide precursor coating with exceptional thermal stability and ductility. Cured polyimide films also have excellent resistance to processing chemicals. As formulated, PI-2545 is made to tight semiconductor specifications, and every lot is fully tested. The product is extremely stable when stored at -18°C. A wet-etch process can used to pattern PI-2545 in conjunction with common positive photo resist and TMAH-based developers. In most applications, PI-2545 should be used with VM-651 or VM-652 adhesion promoter.

12. Technical Service

HD MicroSystems has dedicated technical service facilities in Parlin, New Jersey and Hitiachi City, Japan. Technical support engineers are available through out the world to assist in process development or to help resolve technical problems. For more information contact your regional HD MicroSystems Technical Representative.

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