LASER INTERFEROMETER GRAVITATIONAL WAVE OBSERVATORY

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*LIGO Laboratory / LIGO Scientific Collaboration*

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# Use of PI-2525 Resin with T-9039 Solvent on Vacuum Parts for LIGO


Riccardo DeSalvo,

David Zeb Rocklin


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This is an internal working note
of the LIGO Project.


**California Institute of Technology**
**LIGO Project – MS 18-34**
**1200 E. California Blvd.**
**Pasadena, CA 91125**
Phone (626) 395-2129
Fax (626) 304-9834
E-mail: info@ligo.caltech.edu

**Massachusetts Institute of Technology**
**LIGO Project – NW17-161**
**175 Albany St**
**Cambridge, MA 02139**
Phone (617) 253-4824
Fax (617) 253-7014
E-mail: info@ligo.mit.edu

**LIGO Hanford Observatory**
**P.O. Box 1970**
**Mail Stop S9-02**
**Richland WA 99352**
Phone 509-372-8106
Fax 509-372-8137

**LIGO Livingston Observatory**
**P.O. Box 940**
**Livingston, LA 70754**
Phone 225-686-3100
Fax 225-686-7189


http://www.ligo.caltech.edu/

The purpose of this project is to investigate methods by which a vacuum-safe resin coating can used to manufacture UHV-compatible parts in LIGO. We use poli-hymide resins because of their low outgassing properties. The resin initially used was Cycom 3001, and later the resin PI-2525 was used. Because of their high curing temperature, these polymers can withstand high temperature baking (above 350$^{o}$ C).

These resins have been developed for the silicon microchip industry and as insulating varnish for transformer wires. In these applications the resin is used in very thin films. In LIGO it would be used as coatings to isolate and freeze the windings of actuation and sensing coils. Much thicker layers form, especially between successive windings in a coil. Past tests have shown that the curing process of thick films can cause foaming (in the industry this effect is called Yellow Powder Syndrome. It is generated because the curing process generates water molecules that in thin films can diffuse to the surface and boil off, but in thick films remain trapped in the volume in the form of bubbles). Foaming in the resin is totally unacceptable in UHV environment, as it can trap dirt or liquids (as well as trapping the water and solvent vapor that generate the foaming), which cannot be cleaned or removed.

We investigate different resins, baking profiles, and solutions to produce a smooth, even coating. In particular, we attempt to avoid "Yellow Powder Syndrome," in which baking a resin causes it to break up into a dull powder.

**Solutions:**

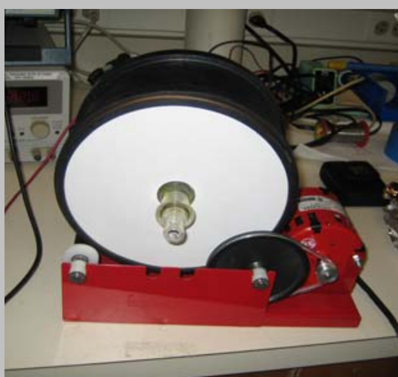
We are testing the resin PI-2525 from Dupont. Prior to that Cycom 3001 was used. The manufacturer's literature [1] suggests dissolving the resin in a solution prior to baking in order to prevent powder formation. As solution, we use the T-9039 thinner from HD Microsystems, composed of n-Methylpyrrolidone and Propylene Glycol Monomethyl Ether [2]. The mixture is approximately 4:1 by volume (the solution and resin have similar densities) in favor of the solution. Jack Craig at Dupont prescribes that, in order to properly dissolve the resins in their solvents, it is necessary to mix them for a couple hours and allow them to sit overnight. The mixing is performed by a modified rock tumbler (figure 1). The tumbler's chamber has been modified to hold a standard glass laboratory bottle, in which the resin and solvent are mixed.

**Figure 1**

Upper Left: The bottle is placed into the modified mixer cavity and held in place by plastic framework.

Lower Left: The cavity is placed on the mixer and rolled by the motor until the solution is well-mixed

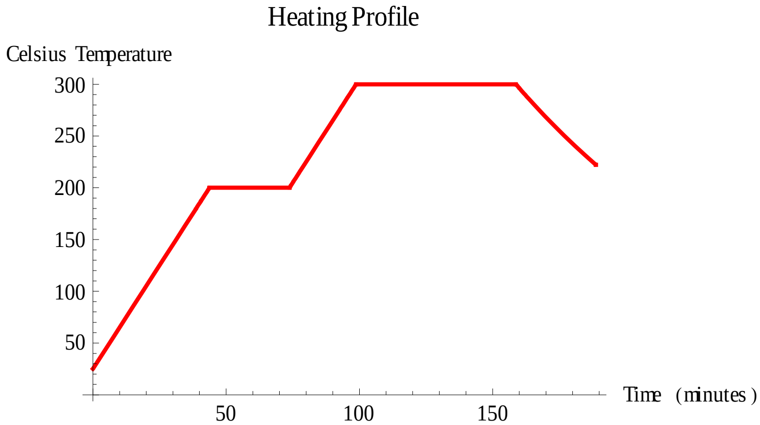
Lower Right: PI-2525 must be dissolved in a special solution—attempting to use



~~**Heating:**~~

~~Heating~~ is done in a programmable oven. The resin is poured into a slanted aluminum tray (the slanting causes a variation in thickness along the sample which, for each sample and heating profile, will allow us to measure the maximum achievable thickness without foaming) and placed in the oven.

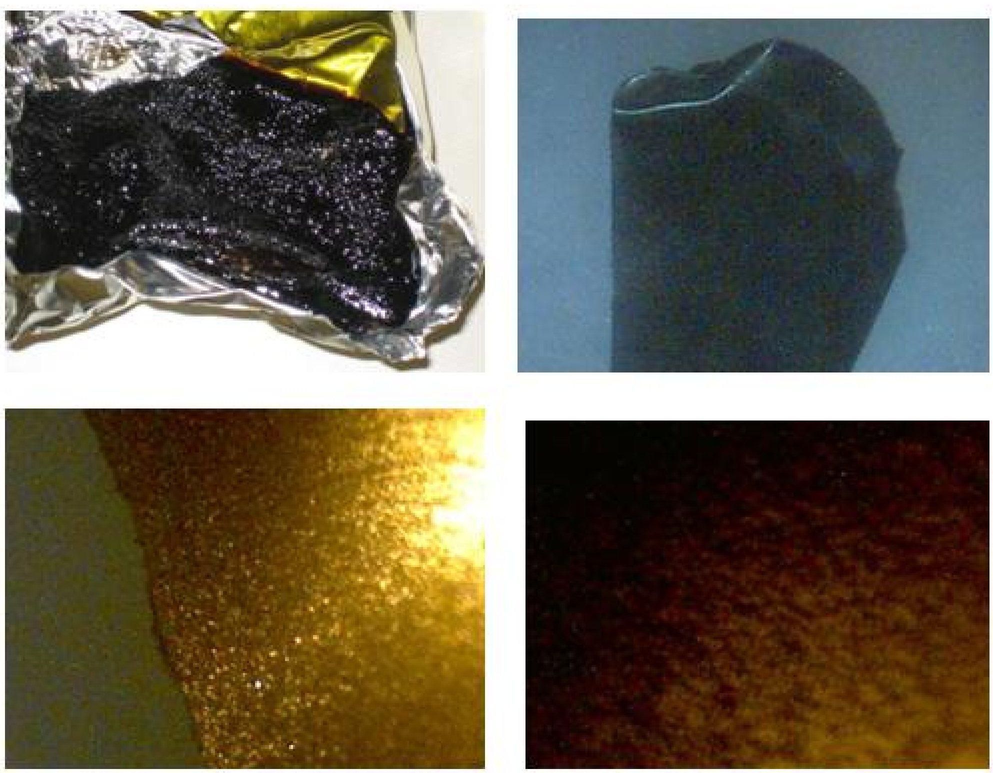
We started with pure resin. The initial heating profile used is diagrammed below. Allowing the sample to cool in between ~~parts~~ of the heating profile does not appear to affect the process.




The initial heating profile used for resin PI-2525

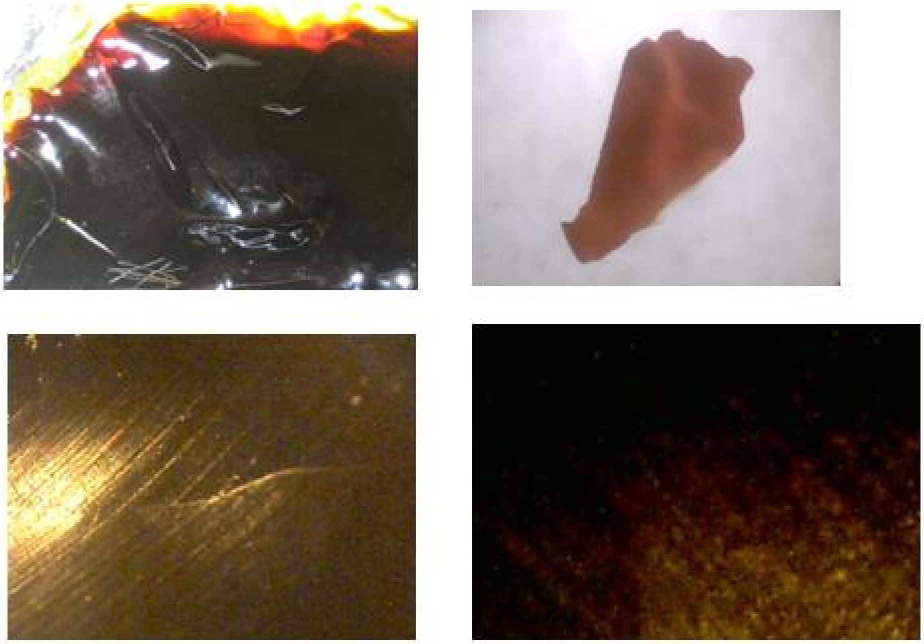
**First Samples:**

The first sample produced (using the above heating profile), generated moderate bubbling, although no powder was present, even below the surface:



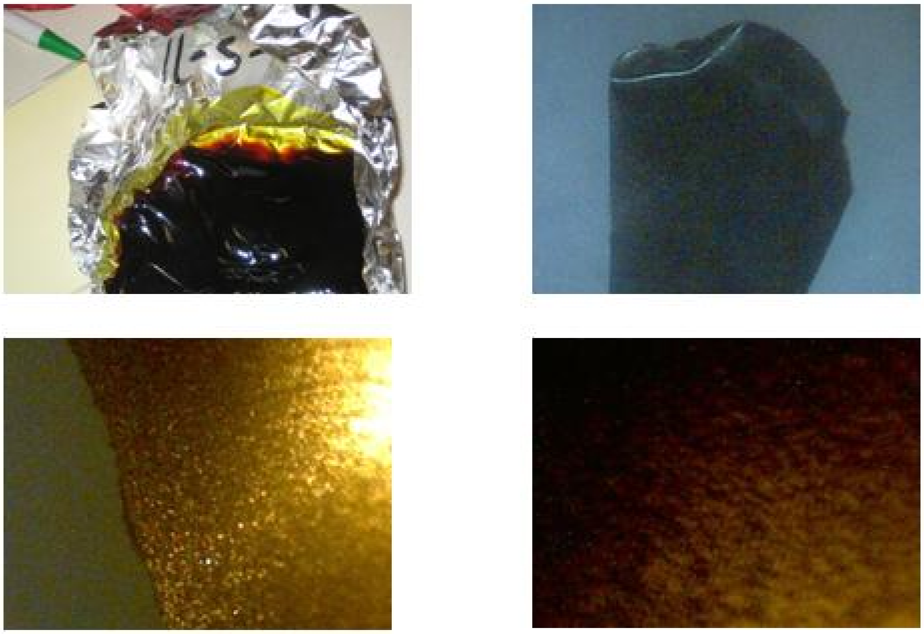
Above: Clockwise from upper left: Normal magnification, 10x magnification, 200x magnification, 60x magnification. Bubbling can be clearly seen, but there is no powdering, and the surface is fairly smooth even at high magnification.

The next sample produced was one with a very slow heating profile, with the entire heating taking 20 hours:



Above: Clockwise from upper left: Normal magnification, 10x magnification, 200x magnification, 60x magnification. While the sample appears very smooth to the naked eye, there are ridges visible at 60x and higher. These may have been produced in removing the sample from its aluminum tray.

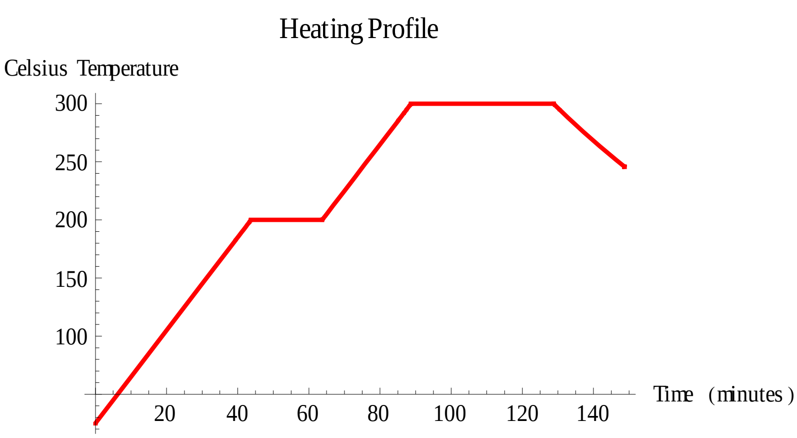
The next sample was run with a relatively modest time budget. Its holds were simply doubled from the original heating profile (60 minutes and 120 minutes). The results were very similar to the second sample:



Above: Top Row—the sample at normal magnification and at 10x. Bottom—the sample at 60x magnification. The sample is very smooth, there do not seem to be any deficits compared to the second sample.

**PI-2525 Resin with T-9039 ~~Solution:~~**

The PI-2525 resin was tested both with and without the T-9039 ~~solution.~~ Several runs were performed, with holds at 200$^{o}$ C and 300$^{o}$ C as short as 20 and 40 minutes respectively:



| | Hold 1 | Hold 2 | Solution | Notes |
|---|---|---|---|---|
| **Run 1** | 60 min | 120 min | No | Good, no bubbling or warping |
| | 60 min | 120 min | Yes | Good, no bubbling or warping |
| **Run 2** | 40 min | 80 min | No | Good, no bubbling or warping |
| | 40 min | 80 min | Yes | Good, no bubbling or warping |
| **Run 3** | 20 min | 40 min | No | Good, no bubbling or warping |
| | 20 min | 40 min | Yes | Good, no bubbling or warping |

The PI-2525 resin proved uniformly superior to the original resin, not exhibiting the Yellow Powder Syndrome. Runs were made with dissolved and undissolved samples together in the oven. The two samples were principally the same. All of the solution ~~dissolved~~ during the baking run. The ~~dissolved~~ sample yielded a somewhat thinner, more evenly distributed finish:




The above samples were created using PI-2525 and the heating profile above. The sample depicted in the two photos on the right was dissolved in T-9039 thinner, and the sample on the left was not. Both samples peel away from the aluminum tray smoothly and without breaking.

Attempts to measure the hardness of the baked resin have proved unsuccessful. The resin is below the hardness which a standard press can measure.

**Recommendation:**

The PI-2525 resin can be effectively cured to parts for use in the UHV environments necessary in LIGO. Based on our tests and the manufacturer's recommendation, we recommend the following formula:

- Thoroughly mix T-9039 and PI-2525 in a ratio of 4:1; allow the mixture to sit overnight.
- Apply the mixture to part and heat in oven:
    - Heat from room temperature to 200$^{o}$ C at 4$^{o}$ C / min.
    - Hold at 200$^{o}$ C for 40 minutes.
    - Increase temperature to 300$^{o}$ C at 4$^{o}$ C / min.
    - Hold at 300$^{o}$ C for 40 minutes.
    - Allow part to cool to room temperature.

- T-9039 must be stored in a chemical safe. PI-2525 should be refrigerated to increase its shelf life.

Notes;
1: The resin can must be brought to room temperature before opening to avoid condensation of water on the resin. To accelerate this process we put the can under a fan.

**References:**

HD Microsystems, "PRODUCT BULLETIN PI-2525, PI-2555, PI-2556 & PI-2574 Polyimide," August 2005

HD Microsystems, "Material Safety Data Sheet: T-9039," December 2004

HD MicroSystems
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PRODUCT BULLETIN

# PI-2545
# Wet Etch Polyimide

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## 1. Introduction

HD MicroSystems' PI-2545 is an established, high temperature polyimide 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 *polyimide* apply. After application the polyimide coating is given a *soft bake* to remove the solvent carrier and partially imidize the film. Positive *photo resist* is applied over the polyimide and *imaged* to define the desired pattern in the underlying polyimide 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 polyimide 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 polyimide apply, 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

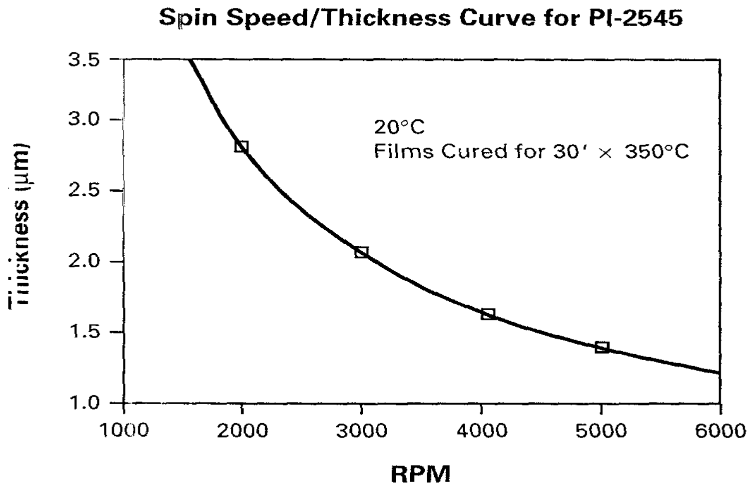
PI-2545 can be coated onto silicon, a variety of metalizations, oxides or other semiconductor and ceramic substrates. An adhesion promoter, should be applied to the substrate prior to polyimide apply. The polyimide solution is viscous. There are some guiding principles for dispensing materials of this 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 polyimide 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 and 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 polyimide 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 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 polyimide 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, a soft bake process is required. The primary objectives are to 1) drive off carrier solvents from the polyimide 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 and develop/polyimide etch.

### 6.6 Choice of Photoresist

Polyimides of this type can be patterned using common positive photoresist. The underlying polyimide 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 coating has minimum solubility in typical photoresist solvents. Photoresist can therefore be coated directly onto the polyimide coating without inter-layer mixing. The polyimide 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 Etch**

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

Polyimide 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 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 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 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 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 the polyimide surface 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 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) | $> 2 \times 10^6$ |
| ▪ 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 removal. Oxygen plasma can be used to remove both uncured 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 coating with exceptional thermal stability and ductility. Cured films also have excellent resistance to both wet and dry-etch 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 Wilmington, Delaware and Hitiachi City, Japan. Technical support engineers are available to work in-house on dedicated process tolls or on location through out the world to assist in process development or t help resolve technical problems. For more information contact your regional HD MicroSystems Technical Representative.


***United States***

**HD MicroSystems, LLC**
P0 Box 80010
Wilmington, DE 19880
800-346-5656 (Phone)
302-892-0597 (Fax)

**HD MicroSystems, LLC**
1333 Lawrence Expressway
Suite 212
Santa Clara, CA 95051
408-260-0880 (Phone)
408-260-0885 (Fax)

***Japan***

**HD MicroSystems, LLC**
10-13, Shibuya 3-chome, Shibuya-ku,
Tokyo 150
Japan
81-3-3407-9003 (Phone)
81-3-3407-9037 (Fax)

**Europe**

**HD MicroSystems Europe GmbH**
DuPont Strasse 1
61343 Bad Homburg
Germany
49-6172-87-1822 (Phone)
49-6172-87-1824 (Fax)

***Internet***
**www.hdmicrosystems.com**

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An Enterprise of Hitachi Chemical and DuPont Electronics

August 2005

PRODUCT BULLETIN

# PI-2525, PI-2555, PI-2556 & PI-2574 Polyimide

PI2525, PI2555, PI-2556 and PI2574 polyimides are suitable for applications where the high cure temperatures typically used for polyimides (350°C) cause problems. Typical applications for these materials are as stress buffer or interlayer dielectric layers over low temperature substrates. These polyimides imidize faster and at lower temperatures than for standard polyimide precursors. The materials are supplied as solutions suitable for spin or roller coating application. A seperate adhesion promoter is recommended with PI-2525, PI-2555 and PI-2556 to improve adhesion to oxides and to metals. PI-2574 is self priming and does not require an adhesion promoter. Processing by wet or plasma etch is possible. Cured film thicknesses from 0.5 µm to 6 µm can be obtained.

## Process Details

### Coating

These products can be coated onto a variety of metals, alloys, semiconductor and ceramic substrates. HD MicroSystems adhesion promoters VM651 or VM-652 are recommended to provide good processability and adhesion with the PI-2525, PI-2555, PI-2556. Bonding of the polyimide to the substrate is achieved during the softbake cycle as the priming chemistry is activated by temperature.

The polyimide solutions are highly viscous. There are some guiding principles for dispensing materials of this type. Always coat substrates which are at room temperature. Never trap air into the solution. This can occur for example when the solution is moved during dispense. All bubbles take time to dissipate out of solution. If left in, coating "comets“ will result. Dispensing should be in the centre and as close to the substrate as possible. A clean cut-off at dispense is neccessary before the spin process starts. It may be neccessary in the case of highly viscous solutions to have a short delay prior to spin to allow the polyimide to flow as far as possible and relax.

Both static and 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 centre of the substrate. Any deviation will result in poor coating quality. The acceleration to final speed should be as low as possible to allow gradual flow of the polyimide 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 the backside contamination potential 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 (see spin speed curves on following page. Longer spin times will improve coating uniformity, but will also reduce the film thickness. In semiconductor applications, an Edge Bead Removal (EBR) and Backside Rinse process may be added to the coating cycle to remove polyimide 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.

### Soft Bake

After application of the polyimide, a bake process is required. Both convection oven and hotplate bake methods may be used. The purpose of this stage is to partially cure the polyimide prior to patterning. This bake stage leaves the polyimide coating dry, yet soluble in the etchant solution.

## Choice of Photoresist

Polyimides of this type can be patterned using common photolithography techniques centered around positive photoresist. The underlying polyimide is an effective anti-reflective layer as there is significant absorption between 350nm and 450nm. 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:

- Compatability 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 2.5 µm film thickness

The polyimide coating after softbake has minimum solubility in typical photoresist solvents. Photoresist can therefore be coated directly onto the polyimide coating without layer inter-mixing occuring.

## Photoresist Application

Substrates should be coated directly with the resist selected. No dehydration bake should be given as this would make the polyimide totally insoluble in the developer. Instead an HMDS vapor prime is permissable if installed on-line but is not really neccessary for good resist adhesion to the polyimide.

Once coated, the resist should be given a softbake at 90°C either in a convection oven for 30 minutes or on a vacuum hotplate for 60 seconds. Once coated and baked, coatings may be held up to 24 hours before exposure.

## Photoresist Exposure

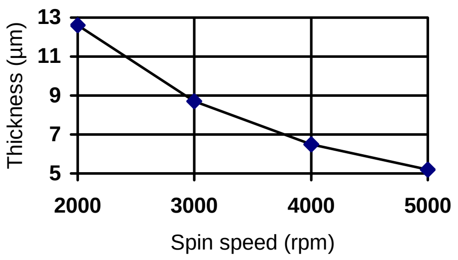
Typical exposure: 50 mJ to 150 mJ

Once exposed, development should take place within 8 hours.

## Spin Speed Curves for Cured Polyimide

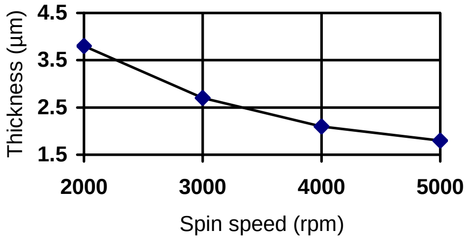
**Pyralin PI 2525/PI2574**

(30 s spin; 120 s at 100°C
Cure: 30 min at 200°C + 30 min at 350°C)



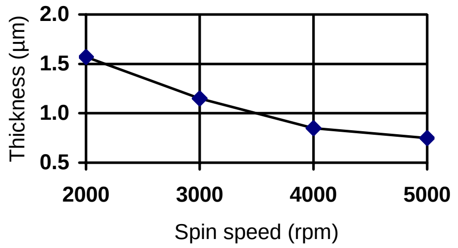

**Spin Speed Curve Pyralin PI 2555**

(30 s spin; 120 s at 100°C
Cure: 30 min at 200°C + 30 min at 350°C)




**Spin Speed Curve Pyralin PI 2556**

(30 s spin; 120 s at 100°C
Cure: 30 min at 200°C + 30 min at 350°C)




## Photoresist Development Polyimide Etch

A single step is used to develop the photoresist and etch the polyimide.

Most alkaline positive resist developers will dissolve both exposed photoresist and polyimide at varying rates. The choice of developer affects the quality of the polyimide image after development. Best results have been obtained using a NaOH based developer.

Thin polyimide layers up to around 5 µm can usually be developed quickly and cleanly with developer which is at ambient temperature. After development of the resist and then the polyimide using a spray puddle technique, a water rinse should be used to remove the developer. The substrate should subsequently be spun until dry.

When thicker polyimide 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 while having minimal effect on the solubility of the photoresist.  In more extreme situations, this may be coupled to a double puddle process.  The second puddle is used to develop only the polyimide layer. Once developed, wafers may be held up to 8 hours before stripping the resist.

## Resist Strip

After developing, the photoresist needs to be stripped off the polyimide surface before curing.  This step is usually carried out on automated track equipment to reduce surface contamination with resist residue which may result if clean solvents are not used.  Resist solvent strippers are normally used.

## Cure

The cure heating cycle converts the polyamic acid to the insoluble imide form and drives out remaining solvent.  This process requires elevated temperatures and controlled environments to achieve the best results.  There is sufficient energy at 180°C to complete the imidization of the polyimide, but higher temperatures are required to completely drive off solvents, thus achieving the ultimate electrical and mechanical properties.  A programmable high temperature oven with typical nitrogen flow rate of 10 litres per minute is recommended for best results.

To activate the adhesion promoter, it is recommended that the cure be carried out up until 200°C in air (min 50% RH).  Above this temperature, a nitrogen atmosphere should be used.  The ramp rates (up and down) should be low to avoid high stress in the polyimide. The maximum cure temperature may be higher than 300°C when the coating is to be subjected to a high temperature process after curing.  In such cases, temperatures up to 400°C have been used to ensure that there is no outgassing during subsequent processes.

## Storage/Shelf Life

Pyralin® PI-2525, PI-2555, PI-2556 and PI-2574 are stable at clean room 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 botttle.

## Example of Typical Process Conditions

**Application of Adhesion Promoter**
**(not required for PI-2574)**
(VM-652 or diluted VM-651)

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

**Apply Polyimide Coating**

- 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 120°C for 30 seconds, followed by 150 °C  for 30 seconds.

**Coat Photoresist**

- Dispense, 3 seconds
- Spread at 500rpm for 5 seconds
- Spin at final speed for 30 seconds
- EBR / Backside rinse, 10 seconds
- Spin Dry for 15 seconds.
- Contact hot plate bake at 90°C for 60 seconds

**Expose Photoresist –** 50mj to 150mj

**Develop Photoresist / Polyimide Etch**
Developer: TMAH, DE-1000, KOH or NaOH
Rinse: DI water
Double Puddle Development Process:

- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Rinse (1000rpm) 15 seconds
- Spin Dry (5000rpm) 15 seconds

**Resist Strip**
Stripper: PGMEA, acetone, N-Butlyacetate

- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Spin Dry (5000rpm) 15 seconds

**Cure (in Nitrogen)**

- Heat from RT to 200°C, ramp rate 4°C/min
- Hold 200°C, 30 minutes
- Heat to 300°C, ramp rate 2.5°C/min
- Hold at 300°C for 60 minutes
- Gradual cooling to RT

## Solution Properties

| | PI-2525/PI-2574 | PI-2555 | PI-2556 |
|---|---|---|---|
| **Solids content (%)** | 25.0 +/-1.0 | 19.0 +/-1.0 | 15.0 +/-1.0 |
| **Viscosity (Poise)** | 60 +/- 10.0 | 14.0 +/-2.0 | 3.5 +/-1.0 |
| **Flash Point** | 93°C | 60°C | 54°C |
| **Solvents (%)** | N-Methyl-2-Pyrrolidone<br>100% | N-Methyl-2-Pyrrolidone<br>Aromatic Hydrocarbon<br>80%/20%±5% | N-Methyl-2-Pyrrolidone<br>Aromatic Hydrocarbon<br>Propylene Glycol Methyl Ether<br>70%/15%/15%±5% |
| **Ash Content (%)** | 0.1 ppm max. | 0.1 ppm max. | 0.1 ppm max. |
| **Chloride Content** | 2.0 ppm max. | 2.0 ppm max. | 2.0 ppm max. |
| **Sodium Content** | 1.0 ppm max. | 1.0 ppm max. | 1.0 ppm max. |
| **Potassium Content** | 0.5 ppm max. | 0.5 ppm max. | 0.5 ppm max. |
| **Copper Content** | 0.5 ppm max. | 0.5 ppm max. | 0.5 ppm max. |
| **Iron Content** | 1.0 ppm max. | 1.0 ppm max. | 1.0 ppm max. |
| **Total Metals** | 10.0 ppm max. | 10.0 ppm max. | 10.0 ppm max. |

## Cured Film Properties

| | |
|---|---|
| Tensile strength ($kg/mm^2$) | 13.1 |
| Elongation (%) | 10 |
| Modulus ($kg/mm^2$) | 245 |
| Stress ($dynes/cm^2$) | $3.6 \times 10^8$ |
| Moisture uptake (%) | 2 - 3 |
| Dielectric constant (at 1 kHz, 50% RH) | 3.3 |
| Dissipation factor | 0.002 |
| Dielectric strength (volts/mil) | 4000 |
| Volume resistivity (ohm-cm) | $10^{16}$ |
| Surface resistivity (ohm) | $10^{15}$ |
| Coefficient of thermal expansion (ppm) | 40 |
| Coefficient of thermal conductivity (cal/(cm)(sec)(°C)) | $35 \times 10^{-5}$ |
| Glass transition temperature | > 320°C |
| Decomposition temperature | 550°C |
| Weight loss (% at 500°C, 120 min) | 2.9 |
| Specific heat (cal/g/°C) | 0.26 |
| Refractive index | 1.70 |


***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.**
Korakuen Building 14F
4-1, Koishikawa 1-chome, Bunkyo-
Tokyo 112-0002, Japan
81-3-3868-8124 (Phone)
81-3-3868-8126 (Fax)

***Europe***

**HD MicroSystems GmbH**
DuPont-Str. 1
61352 Bad Homburg, Germany
49-6172-87-1812 (Phone)
49-6172-87-1824 (Fax)

**Internet**
**www.hdmicrosystems.com**




**Caution:** Do not use in medical applications involving permanent implantation in the human body.