The HD-4100 Series of products is a new negative-tone, solvent developed, photodefiable polyimide precursor for stress buffer and flip chip bonding applications. The HD-4100 Series has the same excellent cured film properties as the HD-4000 Series products but with increased copper compatibility. These two product lines were developed as self-priming, i-line sensitive, photodefiable solutions that can be patterned to cleanly resolve micron scale relief patterns with controlled size and wall profiles without the need for photoresists. They reduce the number of process steps for patterning overcoat layers and are ideal for single mask applications.

HD-4100 Series products have found their greatest applicability in packaging applications. They have excellent mechanical properties to handle the thermal and chemical extremes of post application processing, excellent elongation to prevent cracking, good adhesion (to underfill, UBM’s, metal runners, etc.), smooth sloping via sidewalls and compatibility with copper (no copper migration). They may also be used in traditional stress buffer applications.

**Process Details**

**Coating**

HD-4100 Series products can be coated onto a variety of metals, alloys, semiconductor and ceramic substrates. Bonding of the polyimide precursor to the substrate is achieved during the softbake cycle, as the priming chemistry is activated by temperature. Substrates should be clean and dry prior to use. Oxygen plasma cleaning followed by a wet clean-up with an organic stripper solution to remove organic contaminants is recommended.

The polyimide precursor solutions are highly viscous and care should be taken in dispensing materials of this type. Always coat with the solution and substrate 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 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 in the case of highly viscous solutions to have a short delay prior to spin to allow the solution to flow as far as possible and relax.

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. The recommended spin speed range is 1500–4500 rpms and the recommended spin time is 30–60 seconds.

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 curing. CyP (Cyclopentanone) or NMP (N-methyl-2-pyrrolidone) or NMP/IPA (Isopropyl alcohol) can be used for this purpose.

**Soft Bake**

After application of the polyimide precursor, a bake process is required. The purpose is to drive off carrier solvents to produce a tack free surface for exposure and to provide sufficient chemical resistance and adhesion so that the exposed areas of the coating will not be attacked or delaminated by the developer. Coated substrates should be soft baked on one or more hot plates at 80°C–110°C for 60–240 seconds. Substrates must remain in a horizontal (level) position during the soft bake step since the coating is still liquid after spin application.

Once soft baked, the coated substrates can be stored for up to 48 hours prior to exposure in a wafer cassette box under cleanroom conditions.
Exposure

The amount of exposure energy required for optimum resolution or wall shape depends on the coating thickness, underlying surface reflectivity, structure size and feature uniformity. Most applications use 150 – 400 mJ/cm² I-line. Depth of focus will impact resolution, feature size and sidewall shape. Typical settings are from +2.0 to -5.0µm from the top surface. Broadband exposure can also be used to reduce exposure times.

After exposure, all substrates should be held a minimum of five minutes prior to development for optimal resolution. They also can be stored for up to 48 hours prior to development in a wafer cassette box under cleanroom conditions. Post exposure bakes (PEBs) may lower the exposure energy required. This process works especially well on linked stepper/developer tracks. Typical conditions are 70°C–110°C for 30–90 seconds.

Development

Substrates can be developed using either a spray or puddle process. In the spray process, PA-401D developer is sprayed onto a slowly spinning wafer (1000 rpm) for a set time (20–60 seconds). This is followed by a five second overlap with the rinse and then a complete rinse (5–15 seconds) with PA-400R. The wafer is then spun dry (3000rpm).

In the puddle process, the PA-401D developer is dispensed to form a puddle on a stationary wafer. After a set time (20-80 seconds), the rinse is applied and the wafer is spun dry. A double puddle may be used on thicker films – the developer is applied, spun off, re-applied and then rinsed.

A post-develop bake (PDB) may be used to modify the wall slope. Conditions vary from 150°C–200°C for 60–120 seconds.

Cure

The objectives of a proper cure schedule are to: 1) remove residual solvents, 2) complete the imidization process that changes the precursor into a polyimide, 3) complete the adhesion process, and 4) remove photosensitive ingredients. Curing is performed under a nitrogen environment (oxygen concentration <800ppm) in a diffusion furnace or programmable oven. The temperature ramp rate should be 10°C/minute or below with a 200°C hold for 30 minutes followed by final curing at 375°C for 60 minutes. The furnace can be cleaned with a 700°C cycle for one hour with an air atmosphere.

Spin Speed Curves for Cured Polyimide

Rework

Before curing, HD-4100 Series products can be stripped with commercial cleaners commonly recommended for polyimide precursor removal. Oxygen plasma etching can be used to remove both uncured precursor and cured polyimide. The cured film can also be stripped from Si wafer by HF solution.
Dry Etch Resistance
Both soft baked and cured HD-4100 Series films exhibit high dry etch resistance and are well suited for single-mask wafer overcoat processes. The effects of etch gas composition on film thickness reduction and etch rate are shown in the graph below. The higher the ratio of O2 in the O2/CF4 atmosphere, the larger the film thickness reduction and the higher the etch rate. Even uncured, soft baked films showed good dry etch resistance.

Storage/Shelf Life
HD-4100 Series products are extremely stable. They can be kept at clean room temperatures (21°C) for about four weeks with no significant change in properties. When stored unopened at -18°C, shelf-life is two years from the 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 for HD4100

Apply Coating
- Dispense on static or dynamic substrate
- Spread at 1000rpm for 10 seconds
- Spin at final speed for 30 seconds
- EBR / Backside rinse, 10 seconds
- Spin Dry, 15 seconds
- Hot plate bake at 85°C for 90 seconds, followed by 95°C for 90 seconds.
- Maximum hold time 48 hours

Expose
- 150 to 400mJ/cm², I-line
- 100 to 300mJ/cm², Broadband

Post Exposure
- Hold for 5 minutes minimum
- Optional bake, 80°C for 60 seconds
- Maximum hold time 48 hours

Develop
Developer: PA-401D or PA-400D
Rinse: PA-400R
Double Puddle Development Process:
- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Spray (100rpm) 5 seconds
- Puddle 20 seconds
- Overlap(1000rpm) 5 seconds
- Rinse (1000rpm) 10 seconds
- Spin Dry (3000rpm) 15 seconds

Post Develop Bake (Optional)
- Hot plate bake at 150°C for 2 minutes followed by 200°C for 2 minutes

Cure (in Nitrogen)
- Heat from RT to 200°C, ramp rate 10°C/min
- Hold 200°C, 30 minutes
- Heat to 375°C, ramp rate 10°C/min
- Hold at 375°C for 60 minutes
- Gradual cooling to RT
Solution Properties

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<tr>
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<th>HD-4100</th>
<th>HD-4104</th>
<th>HD-4110</th>
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Cured Film Properties (Typical Data)

- Tensile strength: 200 MPa
- Tg: 330 °C
- Elongation: 45 %
- Modulus: 3.4 GPa
- Coefficient of Thermal Expansion, CTE: 35 ppm/°C
- Decomposition temperature: 600 °C
- Initial (1%) Weight loss: 430 °C
- Residual Stress: 34 MPa
- Dielectric Constant (1MHz): 3.36
- Surface Resistivity (50V): 3.3 X 10¹⁶
- Volume Resistivity (50V): 2.4 X 10¹⁶
- Disipation Factor (1MHz): 0.001
- Dielectric Strength: 250 kV/mm

**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
6326 Neu-Issenburg
Germany
49-6102-18-1823 (Phone)
49-6102-18-1824 (Fax)

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