Molecular Modification of PCB Substrates for Fine Line Patterning

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Next Generation IC Packages

Goal: Multilayer PCB substrate with ~10 micron L/S

Process: Semi-additive (plating and build-up lamination)
Adhesion Issues in Substrates

- Fine line patterning (< 25 um) requires smooth surface
  - Semi roadmap requires ~10um line/space on substrates in 3-5 years
  - Mechanical adhesion insufficient for reliability of fine line traces

- Adhesion mechanism for fine lines will depend on mechanical and chemical forces

<table>
<thead>
<tr>
<th>Existing Approach</th>
<th>New approach</th>
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</thead>
<tbody>
<tr>
<td>Roughened surface</td>
<td>“Smooth” surface</td>
</tr>
</tbody>
</table>
Improving Adhesion in Substrates

- Chemical composition of surface depends on many factors
  - Material composition
  - Curing conditions
  - Storage history
  - Chemical treatments (cleans, desmear, etc.)

- Selection of adhesion chemistry
  - Stable chemistry (i.e., good shelf life, reproducibility)
  - Wide process window (time, temperature, concentration)
  - Broad application to many substrates
Molecular Interface

- Molecules can attach “incompatible” materials
- Copper can be attached to epoxy
- Epoxies, resists, etc. can be attached to copper
- Chemistry engineered for specific material properties

~ 1 nm
Summary of ZettaCore feasibility studies

• Porphyрин molecules have survived exposure to various electroplating solutions
  • Cu plating demonstrated on a variety of substrates
  • Enhanced peel strength correlates with good porphyrin coverage
• Porphyрин survives Cu metal deposition
  • Porphyrin configuration does not change significantly in Cu film
  • Metal structure of Cu film on top of porphyrin monolayer is as smooth as underlying Si (100) structure
ZettaCore Chemistry: Initial Work

X: Cu, Pd-binding component
Y: Surface reactive component
Z: Surface leaving group
Molecule / Process Development

- Identification of reactive components
  - Chemical characterization of target substrates
  - Identification of reactive chemical species on surface
- Molecular design and synthesis
  - Design of reactive intermediates for attachment to selected surface
  - Id or synthesis of desired molecules and chemical characterization
- Molecule attachment and characterization
  - DOE on attachment conditions (time, temperature, concentration)
  - Method development for surface characterization
- Copper deposition / Lamination evaluations
  - Electroless plating / Electroplating
    - or -
  - Lamination
Overview: Molecule-enhanced Cu²⁺ plating

Epoxy

Molecule Reaction

Catalyst Reduction & Nucleation

Porphyrrins forms a complex with Pd²⁺ catalyst

Electroless Cu²⁺ reduction and adhesion

Lamination

Cu Plating
Molecule Optimization

- Utilize a stable molecular platform
- Each site can perform different function
  - Individually optimized for specific function
  - Failure analysis possible for each function
- Systematic building block approach
  - Isolate the chemistry needed for specific function
  - Each site can be optimized independently and systematically
- Allows root cause failure analysis and complete characterization
  - Allows rational design and optimization of each molecular component
  - Preserves flexible design that can be modified & optimized as conditions change

**R for carbon substrates**
Numerous C-C linkages can be formed with existing chemistries

**X for Cu substrates**
Numerous chemistries tested and available for use

![Molecular structure diagram]
ZettaCore MI Process for Cu Plating

Molecule Attachment

- Substrate Cleaning
- Molecule Deposition
- Baking Attachment
- Rinse & Post Treatment

E-less Cu Plating

Pre-anneal

Electrolytic Cu Plating

Post-anneal

Testing

- Peel Strength Test
- HAST
- Repeat Peel Test

Standard Chemistries Employed
No need for changes in standard processes!!!
Correlation of porphyrin and Pd distribution on surfaces

- Porphyrin molecules distribute uniformly on the epoxy surface
- Pd catalyst distributes uniformly on top of porphyrin
Cross-sectional SEM of E-less Cu deposition

Eless-Cu: @ 30°C

Roughened surface

10min.

20min.

40min.

Porphyrin attached smooth surface
Optimization of Molecule Properties

1. Identify reactive components
2. Does an existing linker work?
   - Yes: Molecule attachment and optimization
   - No: Synthesize/optimize new linker/process
3. Molecule attachment and optimization
4. Copper deposition
5. Peel strength adequate?
   - Yes: Reliability testing
   - No: Copper deposition
6. Reliability testing
   - Fail: Peel strength adequate?
   - Pass: Reliability testing
Demonstration of Peel Strength on Planar Substrates

- Demonstration of peel strength pre-HAST testing
  - 0.62 ± 0.02 Kg/cm on smooth surface, better than roughened control

Smooth substrate
0.62 ± 0.02 Kg/cm

Roughened control
0.60 ± 0.02 Kg/cm

Without Treatment
# Summary: Impact of Molecular Layer for Copper on Epoxy – Reliability Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Test conditions</th>
<th>Success criteria</th>
<th>Result /Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel strength</td>
<td>Peel width 1.0 cm, speed 5.0 cm/min at 90 degree angle</td>
<td>Roughened control (~0.6 Kg/cm)</td>
<td>0.62 Kg/cm</td>
</tr>
<tr>
<td>Reflow and HAST</td>
<td>Pre-conditioning (Level 3): 125°C – 25 hr, 30°C/60%RH – 192 hr&lt;br&gt;Reflow: 260°C 3 times&lt;br&gt;HAST: 130°C, 85%RH – 96 hr</td>
<td>Peel strength degradation ≤ roughened control</td>
<td>10% degradation vs. 13% for roughened control</td>
</tr>
<tr>
<td>Extended Bake</td>
<td>165°C – 504 hr</td>
<td>Peel strength degradation ≤ roughened control</td>
<td>No degradation</td>
</tr>
<tr>
<td>Thermal Cycle</td>
<td>Pre-conditioning (Level 3)&lt;br&gt;Reflow: 260°C 3 times&lt;br&gt;TC (cond. C): -65°C to 150°C, dwell 15 min, 1000 cycles</td>
<td>Peel strength degradation ≤ roughened control</td>
<td>No degradation</td>
</tr>
<tr>
<td>Thermal Shock</td>
<td>Preconditioning (Level 3)&lt;br&gt;Reflow: 260°C 3 times&lt;br&gt;TS (condition C): -65°C to 150°C, dwell 5 min, 1000 cycles (in liquid)</td>
<td>Peel strength degradation ≤ roughened control</td>
<td>4% degradation vs. 8% for roughened control</td>
</tr>
<tr>
<td>THS</td>
<td>85°C, 85%RH – 1000hr</td>
<td>Peel strength degradation ≤ roughened control</td>
<td>9% degradation - same as control</td>
</tr>
</tbody>
</table>
Plating: Enabling Fine-line patterning

Patterned structures
Patterning completed on ZettaCore processed substrates to L/S of 8um

<table>
<thead>
<tr>
<th>L/S</th>
<th>Customer A</th>
<th>Customer B</th>
<th>Customer C</th>
<th>Customer D</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50um</td>
<td>Pass</td>
<td>Pass</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>30/30um</td>
<td>Pass</td>
<td>Pass</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>20/20um</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>N/A</td>
</tr>
<tr>
<td>18/18um</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>N/A</td>
</tr>
<tr>
<td>14/14um</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>N/A</td>
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<tr>
<td>12/12um</td>
<td>Pass</td>
<td>TBD*</td>
<td>Pass</td>
<td>N/A</td>
</tr>
<tr>
<td>10/10um</td>
<td>Pass</td>
<td>TBD*</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>8/8um</td>
<td>Pass</td>
<td>TBD*</td>
<td>TBD*</td>
<td>Pass</td>
</tr>
</tbody>
</table>

* Requires etch / process modification

Confirms value of ZettaCore technology in enabling advanced geometries
Adhesion Issues in Lamination on Copper

- Fine line patterning (~10 um) requires smooth Cu surface
  - Mechanical adhesion insufficient for reliability of fine line traces
  - Conventional Cu roughening processes provide insufficient adhesion

- Adhesion mechanism for fine lines will depend on mechanical and chemical forces

Existing Approach

Roughened Cu surface

New approach

“Smooth” Cu surface
Optimization of Molecule Properties for Adhesion in Cu Lamination Process

Identify reactive components

Does an existing molecule work? No → Synthesize/optimize molecule/process

Yes → Molecule attachment and optimization

Epoxy Lamination

Peel strength adequate? No → Fail

Yes → Reliability testing

Pass

Yes → Molecule attachment and optimization
ZettaCore MI Process for Cu Lamination

Molecule Attachment
- Surface Cleaning
- Surface Conditioning
- Surface Treatment
- Baking

Lamination
- Standard Chemistries/Processes
  No need for changes in standard processes!!!

Testing
- Peel Test
- HAST
- Repeat Peel Test
SEM of Smooth and Mi™-treated Copper Surfaces

After HAST and Peel-back of laminated Epoxy

Untreated Smooth Cu

Surface is clean Cu suggesting that the peeled surface breaks at the Cu-resin interface.

Mi™ - Treated Cu Surface

Most areas covered by resin suggesting Cu-resin interface breaks within the resin, not at the Cu-resin interface.
Lamination: Peel Strength Data

**Table:**

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Peel Strength (Kg/cm)</th>
<th>Roughness (R_a, μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>96 hr HAST</td>
</tr>
<tr>
<td>Roughened</td>
<td>1.15</td>
<td>0.74</td>
</tr>
<tr>
<td>Smooth</td>
<td>0.50</td>
<td>0.07</td>
</tr>
<tr>
<td>Smooth w molecule</td>
<td>1.18</td>
<td>0.93</td>
</tr>
</tbody>
</table>

**Graph:**

- **Legend:**
  - Initial
  - 96 hr HAST

**Notes:**

- **Desired combination**

*ZettaCore treatment shows superior HAST stability – 21% degradation vs. 36% for roughened control*
**Solder Resist: Paste and Dry Film Processes**

### Paste SR Process
- **Smooth Cu Foil**
- Pre-clean (NaOH / soft-etch / acid clean)
- MI treatment
- MI treatment layer
- Solder Resist (SR coating / baking / UV / develop / UV / post-bake)
- Solder Resist
- Lamination (GX-13 / backing board / curing)
- backing substrate
- ABF
- Peel strength measurement
- Reliability Test (Reflow / 48 and 96-hrs HAST)

### Dry Film Resist Process
- **Smooth Cu Foil**
- Pre-clean (NaOH / soft-etch / acid clean)
- MI treatment
- MI treatment layer
- Solder Resist (SR dry-film lamination / UV / baking / UV)
- Solder Resist
- Lamination (3X GX-13 / backing board / curing)
- backing substrate
- ABF
- Peel strength measurement
- Reliability Test (Reflow / 96-hrs HAST)
Solder Resist: DFR Material Summary

ZettaCore treated smooth Cu shows superior HAST stability and No undercut or delamination after subsequent processing (soft-etch and Ni/Au plating)
Lamination: Results Summary

Peel strength and HAST stability:
• 1.33 Kg/cm before and 1.15 Kg/cm after HAST
• 14% degradation vs. 36% for roughened control

Lamination and HAST stability on patterned Cu lines:
• ZettaCore process does not roughen the Cu lines
• No delamination after HAST
• Isolation resistance > $10^{12}$ $\Omega$ after HAST

Laser drilling and via clean/plating compatibility:
• No delamination or undercut post via-clean and plating

_ZettaCore process enhances adhesion without roughening the Cu surface_
_Demonstrated through HAST testing_
MI Results Summary

- ZettaCore solutions available for all 3 interfaces
  - e-less plating on smooth dielectric
  - resin lamination on smooth copper
  - solder resist on smooth copper

- Provides finer line dimensions and improved reliability performance