Impact of Molecular Interface on Copper after Epoxy Lamination and HAST testing

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It is essential to achieve good adhesion between a smooth copper circuit layer and resin insulation layer in multilayer PWB structures. ZettaCore has developed a molecular interface (MI) layer that provides adhesion without roughening the surface. The copper surface is modified with a molecular reagent that promotes adhesion to the subsequently applied dielectric layer, a commercially available smooth epoxy resin (Ajinomoto ABF-GX13 and GX-92), using a reaction to functionalize the metal and provide adhesion sites in a single step. The resulting surface film exhibits desirable properties without the need for post processing. This reduces the complexity of the process and provides significant cost savings. Examination of the treated surfaces with peel tests and cross sectional views after reflow and HAST demonstrates the robustness of the new process.

A molecular functionalization layer is formed on top of the metal to provide adhesion sites. This is facilitated by chemical bonding of the surface to create a functionalization layer containing an organic molecular layer. In the MI process, the smooth metal-resin interface possesses superior adhesion strength and resistance to heat, moisture, and chemical attacks compared to the untreated smooth surface, and in many cases, superior performance than the roughened copper-resin interface.

**EXPERIMENTAL & RESULTS**

The experimental process comprises four major steps: (1) surface pre-treatment, (2) MI treatment, (3) vacuum lamination, and, (4) heat treatment (if necessary). Surface pre-treatment is carried out by conventional alkaline clean, rinsing, soft etching and acid clean, rinsing and drying the substrate. Functionalization may then occur, followed by rinsing and drying the substrate.

**Treatment of Copper Surface**

An electrolytic copper substrate was first cleaned with sodium hydroxide solution at 50 °C for 2 minutes, and then rinsed with water. The copper substrate was further cleaned in hydrogen peroxide solution (at RT for 1 minute), and sulfuric acid solution at RT for 1 minute, and then followed by water rinse. The copper was then functionalized by treatment with MI process followed by water rinse. The sample was then rinsed and dried by hot air.

**FIGURE 1A**

**FIGURE 1B**

**FIGURE 1C**

**FIG. 1A** is an exemplary SEM micrograph showing the typical morphology of a conventional electrolytic copper surface (i.e. a smooth copper surface that has not been intentionally roughened). In comparison, the morphology of an electrolytic copper surface treated using ZettaCore’s MI chemistry is shown in **FIG. 1B**. As is very apparent, the MI layer on the treated copper surface shown in **FIG. 1B** exhibits a similar morphology and greater uniformity. By contrast, **FIG. 1C** shows a conventional black oxide surface which exhibits a much rougher structure. The data of **Table 1** compares the surface roughness expressed in both R\(\alpha\) and R\(z\), and demonstrates that the MI process does not roughen the copper surface, unlike conventional oxidation and reduction processes, which roughen the surface considerably.

<table>
<thead>
<tr>
<th>Roughness</th>
<th>As-plated smooth Cu</th>
<th>Treated smooth Cu</th>
<th>Black oxide roughened Cu</th>
<th>Micro-etch roughened Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(\alpha) (µm)</td>
<td>0.13</td>
<td>0.14</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td>R(z) (µm)</td>
<td>1.31</td>
<td>1.45</td>
<td>5.20</td>
<td>4.50</td>
</tr>
</tbody>
</table>

**Demonstration of the enhancement of resin bonding on a smooth copper substrate**

The above-mentioned treated Cu test strips were laid out on a temporary backing. A commercial epoxy laminate film (ABF-GX13 or GX92) of 35 µm thickness was laid on top of the Cu strips. The assembly was then vacuum
laminated at 100 °C, 30-s vacuum, and 30 s press at 4 Kg / cm². The lamination step was repeated twice to form a total of 3 plies of ABF films. A rigid backing substrate of the same type of material was laminated on top of the ABF film to allow quantification of adhesion strength. The assembly was then cured in a convection oven at 180 °C for 90 min. Next the assembly was diced to remove the temporary backing substrate and separate into individual test coupons for peel strength testing and testing using the highly accelerated stress test (HAST). The adhesion strength of the resulting laminate was quantified by a force gauge of a peel tester on a peel strip of 10 mm width at a 90 degree peel angle and peel speed of 50 mm/min. Specifically, peel strength was tested on the substrates as initially formed, and then after preconditioning and reflow and HAST.

The lamination conditions used were as specified by Ajinomoto, and the thermal profile of the sample (lamination process, preconditioning, reflow and HAST) did not impact the stability of the MI layer, as indicated by the retention of peel strength. This was confirmed by optical inspection before and after each thermal exposure.

**Stability of resin bonding on a smooth copper substrate after HAST**

Preconditioning was carried out at 125 °C for 25 hours, followed by 30 °C and 60% relative humidity (RH) for 192 hours. Reflow was carried out three times at 260 °C. Thereafter, HAST testing was conducted at 130 °C and 85% RH for 96 hours. **FIG. 2** illustrates the impact of the treatment on the peel strength retention of GX92 post HAST testing. The smooth control without (i.e. without a MI layer) dropped 90% in peel strength post HAST, and the conventional roughened control showed a 57% loss.

**FIGURE 2**

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Peel Strength (Kg/cm)</th>
<th>Roughness (Ra, µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughened</td>
<td>0.89</td>
<td>0.38</td>
</tr>
<tr>
<td>Smooth control</td>
<td>0.87</td>
<td>0.08</td>
</tr>
<tr>
<td>Treated smooth Cu</td>
<td>1.13</td>
<td>0.15</td>
</tr>
</tbody>
</table>

In contrast, the treated smooth copper substrate (i.e. with the MI layer) showed not only higher initial peel strength but also a higher retention of adhesion strength (only 11% loss). The tabular data of **FIG. 2** also demonstrate that the enhancement in peel strength stability was achieved without a significant change in the surface roughness.

**FIGs. 3A and 3B** are exemplary SEM micrographs of peeled copper surfaces showing that the copper-resin interface breaks right at the copper surface for a smooth copper control (**FIG. 3A**), whereas the interface breaks within the resin (cohesive failure) for the MI treated smooth copper surface (**FIG. 3B**) formed according to methods of the MI process. Some areas are covered with a thin layer of conformal epoxy, as confirmed with EDX spectroscopy. The result demonstrates that the bonding strength between the resin and the treated copper surface treated with the MI process is stronger than the bonding strength within the bulk resin materials themselves.

**CONCLUSIONS**

The efficacy of the new MI process has been demonstrated on epoxy substrate materials. A dramatic increase in the adhesion of a laminated epoxy was demonstrated to smooth copper metal, and the adhesion was stable to lamination process, preconditioning, reflow and HAST. These surfaces showed even less degradation in peel strength than the roughened controls, and that the interface created in this process is even more stable than the bulk epoxy materials.