Molecular Modification of PCB Substrates: Demonstration of HAST Survivability of Fine-Line Patterned Structures

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Abstract

The present work describes the use of a molecular adhesion layer on smooth PCB substrates to facilitate the electroless deposition and electroplating of copper. Molecules are attached to smooth ABF-GX13 substrates via a thermally-induced reaction of the molecular species with the ABF-GX13 surface. The high affinity of the molecule-modified surface for metal ions facilitates electroless plating of the copper, which is then used as a seed layer to electroplate thicker copper layer utilizing conventional procedures. A molecule is attached to the epoxy surface of the ABF-GX13 substrate. The formation of a molecular layer on the epoxy surface is identified by mass spectrometry and characterized by fluorescence and UV absorbance spectroscopy. The molecule coverage is proportional to the fluorescence signal, increases with increase in attachment concentration and temperature. Once the molecular layer is formed on a smooth (unroughened) ABF-GX13 epoxy substrate, the treated substrate is subjected to standard electroless Cu deposition processes. After subsequent electroplating, the adhesion strength of the resulting Cu film is quantified by a peel tester. The molecule-coated smooth ABF-GX13 substrate showed a roughness (Ra) less than 0.2 µm and the plated Cu showed peel strengths comparable to that measured for the roughened control substrate. Patterned structures, including fine lines and vias, were formed and reliability tests were performed to determine the robustness of the copper/molecular interface under a variety of stress conditions including reflow, HAST, TC, TS, and extended bake. The molecule attached smooth samples showed comparable degradation in peel strength after the stress tests compared to conventionally desmeared and roughened samples. This demonstrates that it is possible to achieve high adhesion strength and reliability by molecular bonding on a smooth ABF-GX13 surface and create fine-line patterned copper traces using this conventional epoxy substrate.

Introduction

Many techniques have been described to chemically modify surfaces with organic or organometallic molecules via reaction with specific functional groups.[1-6] For example, when a surface containing hydroxyl groups or amine groups is available, it may be reacted with isocyanate, siloxane, acid chlorides, etc. When the surface does not include any functional groups that can be reacted with available reagents, the surface may be pretreated with a wide variety of chemistries, ranging from solvent washes to extensive oxidation of organic materials. This yields a surface where one of the remaining functional groups is compatible with one of the reagents used for surface modification. From this point of view, it is found that the modification of a surface is merely a particular case of organic chemistry reactions, in which one of the two reagents is a surface rather than a molecule in solution.

The kinetics associated with heterogeneous reactions between a solution and a surface are substantially different from the analogous reaction in a homogeneous phase, but the reaction mechanisms are identical in principle. In many cases, the surface is activated by pretreating it so as to create functional groups with higher reactivity, so as to obtain a faster reaction. These may be unstable functional groups, formed transiently, for instance radicals formed by vigorous oxidation of the surface, either chemically or via irradiation. These methods are only useful when the

surface to be treated has an electronic structure similar to that of an insulator, i.e., the surface needs to have localized states. However, when the surface is a conductor or an undoped semiconductor, such localized states do not exist: the electronic states of the surface are delocalized states. Therefore, it is much more difficult to use the same organic chemistry reactions to attach an organic molecule of interest onto a metallic surface. Several examples do exist: these are the spontaneous chemical reactions of thiols, and of isonitriles described on metal surfaces, and especially on gold surfaces. However, these reactions cannot be exploited in all situations. Specifically, thiols, for example, give rise to weak sulphur/metal bonds. These bonds are broken when the metal undergoes cathodic or anodic polarization, such that they form thiolates and sulphonates, respectively, which desorb.

One way to increase the stability of the modified surface is to begin with more stable reagents and produce more stable bonds. Unfortunately, more stable reactants only undergo significant reaction when the reaction rate is accelerated (typically, by raising the temperature of the reaction). The acceleration of the kinetics of the reaction can be quite dramatic; for example, raising the temperature of a reaction by 100 C can result in completion of a reaction within minutes, when it was virtually unreactive at room temperature. The only constraint on the process is that the reaction temperature may not exceed the temperature at which either the functionalizing molecule or the substrate itself will decompose chemically. Thus, if one can find thermally stable, reagents to use for surface modification, a wide variety of chemical reactions that heretofore were not available for surface modification become available. It also allows the modification of a large number of substrates that were not considered reactive previously. The result is a new paradigm for the surface modification of materials that can be used in a large number of situations.

Printed circuit boards (PCB) are widely used for packaging of integrated circuits and devices. As device densities increase, high density package designs such as multi-layer structures are becoming increasingly important, which present additional design challenges. As circuit densities increase, the widths of contacts, vias, lines and other features, as well as dielectric materials between them, decrease. This requires that the surface of the PCB remain smoother, which makes the adhesion of the adjacent layers cannot depend on traditional roughening processes. This becomes even a greater challenge when the composition of the PCB is examined. Typically, it comprises a polymer material, such as an epoxy, a substantial amount of a filler material, such as glass, silica, or other materials. Introduction of a molecular species on its surface as a chemical adhesive material, such as a porphyrin, must substantially alter its chemical affinity for a metal, such as copper, in order to facilitate strong adhesion between the polymer composite and the metal layer without significantly roughening the surface. Once the copper layer is deposited and patterned, a second layer of the chemical adhesive layer may be applied to the copper surface to promote adhesion between it and subsequent polymer (epoxy/glass) layers. In a multilayer conductive structure, this process may be repeated several times on both sides of the core material.

RESULTS AND DISCUSSION

Attachment of organic molecules onto a ABF-GX13 substrate. A commercial smooth epoxy resin (Ajinomoto ABF-GX13) substrate was first cleaned by sonication for 5 minutes in water and then isopropyl alcohol. The substrate was coated with a solution containing 0.1 to 1 mM of the molecule solution in an appropriate solvent (e.g., isopropanol, hexane, toluene, and the like) by either spray-coating, dip-coating, drop-coating, or spin-coating. The sample was then baked at 70 to 200 $^{\circ}$C for 5-20 minutes and followed by standard surface cleaning processes to remove the residual unattached molecules (**FIG. 1**). The amount of molecule attached can be adjusted by varying the concentration of the molecule, the attachment temperature, and duration, and monitored by UV absorption spectroscopy as illustrated in **FIG. 2**. As illustrated in **FIG. 2 (Top)**, the UV adsorption strength is proportional to the molecule coverage which increases with increase in attachment concentration. Additionally, molecule coverage increases with increase in attachment temperature as shown in **FIG. 2 (Bottom)**.

Demonstration of the robustness of molecule layer on an ABF-GX13 epoxy substrate. Following molecule attachment and surface cleaning processes, the epoxy substrate was subjected to electroless Cu deposition in the following manner (**Figure 3**): (a) the substrate was immersed in Shipley/Circuposit Conditioner 3320 for 10 min at 65 °C followed by DI water rinse at 65 °C for 2 min, (b) immersed in Shipley/Cataposit Catalyst 404 (Pre-dip) at 23 °C for 1 min and then in Shipley/Cataposit Catalyst 44 (Activation) at 40 °C for 5 min followed by DI water rinse at 23 °C for 2 min, (c) immersed in Shipley/Accelerator 19E (Acceleration) at 30 °C for 5 min followed by DI water rinse at 23 °C for 2 min, (d) immersed in Shipley/Cuposit 328L Copper Mix (E-less Cu) at 30 °C for 40 min followed by DI water rinse at 23 °C for 2 min and blow dry with air at 23 °C for 1 min. The sample was then annealed in air at 170 C for 30 min.

The electroless film was evaluate by tape peeling and characterized by microscopy shown in **FIG. 4**. The tape peeling test provides a qualitative characterization of the peel strength of the copper layer and is generally performed to test the electroless copper layer. **FIG. 4** shows photographs of test coupons of ABF-GX13 substrates having electroless copper formed thereon along with a control test coupon which was prepared without molecular treatment. As shown in **FIG. 4**, the molecule-treated surface provides a good substrate for plating and enhances copper adhesion to the smooth epoxy surface. **FIG. 4** further illustrates that the molecules also reduce the defect density therefore promoting the adhesion between copper and the ABF-GX13 epoxy substrate.

Electrolytic Cu deposition. Electrodeposition was applied to the electroless Cu covered substrate to increase the thickness of copper up to 25~50 µm for peel strength evaluation. The ABF-GX13 substrate was first cleaned in 1 M sulfuric acid, then electroplated in Shipley/Copper Gleam ST-901 Acid Copper at 20 mA cm^{-2} at 23 °C for 90 min, followed by DI water rinse at 23 °C for 2 min and blown dry with air at 23 °C for 1 min. The sample was then annealed in air at 170 °C for 120 min. Next, peel strength is tested on the electrolytic copper layer. **FIG. 5** illustrates that the peel strength of the electrolytic copper on molecule attached surface is increased by a factor of 60 compared to the control without molecule attachment. Surface imaging of the ABF-GX13 substrate shows insignificant change in the surface roughness (Ra) and morphology of the surface during this process. The difference in surface roughness between roughened and smooth, molecule treated substrates is shown in cross-sectional SEM's in **Figure 6**.

Reliability Testing. A number of experiments were performed to test the reliability of copper layers on molecule-treated ABF-GX13 substrates under a variety of stress conditions. The results are summarized in **Table 1** and described in detail below.

The copper-plated, molecule-treated smooth ABF-GX13 substrates were subjected to Highly Accelerated Stress Testing (HAST) testing at various intervals and then tested for peel strength. The peel strength was tested as described above. Specifically, peel strength was tested on the substrates as initially formed, and then after preconditioning and reflow. Preconditioning was carried out at 125 °C for 25 hours, followed by 30 °C/60% RH for 192 hours. Reflow was carried out three times at 260 °C. Thereafter HAST testing was conducted after 96 hours and 192 hours. As shown in **Table 1**, the copper-plated, smooth molecule-treated ABF-GX13 substrates showed only slight peel strength degradation after 96 hour HAST testing (less than 10%), whereas the roughened control substrate suffered peel strength degradation of 13%.

Copper-plated, molecule-treated smooth ABF-GX13 substrates were thermally aging by extended baking at 165 °C, and then tested for peel strength at different time intervals. As demonstrated in **Table 1**, smooth molecule-treated ABF-GX13 substrates did not exhibit any peel strength degradation after 1008 hours of thermal aging.

Identically treated copper plated ABF-GX13 substrates were also subjected to thermal cycles (TC) as shown in **Table 1**. The substrates were subjected to thermal cycles over a temperature range of -65 °C to 150 °C for a dwell time of 15 minutes, for a total of 1000 cycles. These substrates exhibit insignificant degradation in peel strength after 1000 cycles.

Similar copper-plated ABF-GX13 substrates were also subjected to thermal shock (TS) testing as shown in Table 1. The substrates were subjected to thermal cycles in liquid over a temperature range of -65 ℃ to 150 ℃ for a dwell time of 15 minutes, for a total of 1000 cycles. These devices exhibited insignificant degradation in peel strength after 1000 cycles. Specifically, these devices exhibit only 4% degradation in peel strength after 1000 cycles, while the control substrate exhibits 8% degradation after 1000 cycles.

Fine Line Patterning. Devices formed above were then further processed to demonstrate that patterning of fine lines is enabled by the present invention. Specifically, smooth ABF-GX13 substrates were treated as described above, to the point where electroless copper was deposited to a height of approximately 0.5 micron. At that point, standard lithographic processes using the semi-additive patterning process[7] were employed to create comb patterns of lines and spaces with equal dimensions (e.g., 50/50, 30/30, 20/20, 18/18, 14/14, and 8/8 microns). An example of a fine line patterned structure is shown in **Figure 7**, where a top-down SEM of the patterned lines is given. Good results were obtained on all of these structures using a variety of patterning conditions and processes, indicating that treatment with the molecular adhesion process significantly improved the ability to pattern copper lines at fine line spacing (**Table 2**). Patterned structures, including fine lines and vias, were formed and reliability tests were performed to determine the robustness of the copper/molecular interface under a variety of stress conditions including reflow, HAST, TC, TS, and extended bake. The molecule attached smooth samples showed less degradation in peel strength after the stress tests compared to conventionally desmeared and roughened samples. This demonstrates that it is possible to achieve high adhesion strength and reliability by molecular bonding on a smooth surface and create fine-line patterned copper traces using an ABF-GX13 epoxy substrate.

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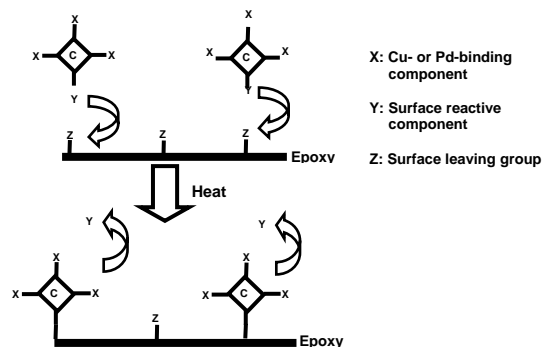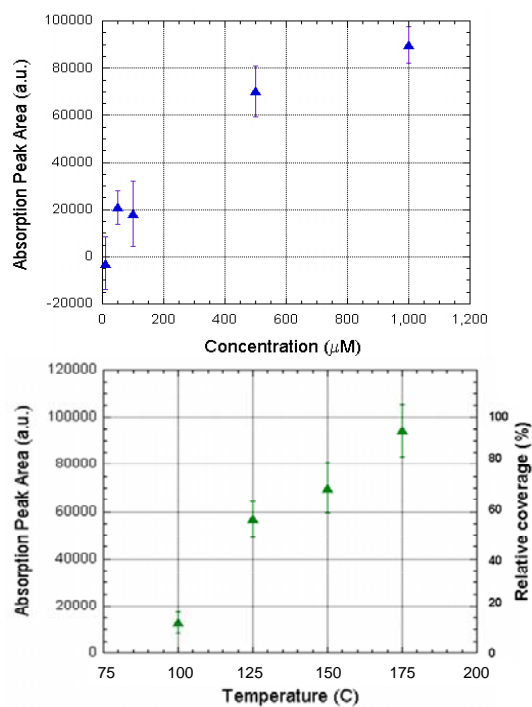
Figure 1: Molecule attachment process.

Figure 2. *Top*: Effect of attachment temperature on molecule coverage; *Bottom:* Effect of molecule concentration on molecule coverage as measured with reflective absorbance spectroscopy.
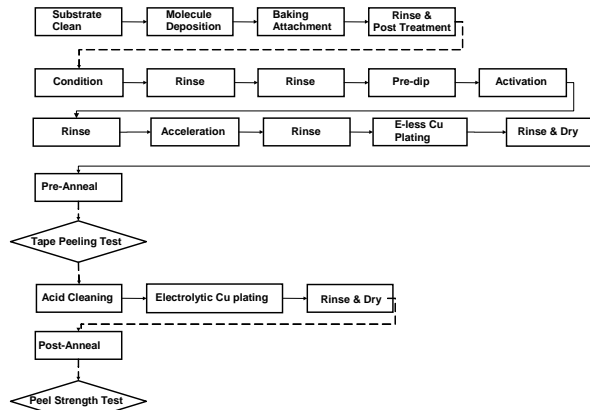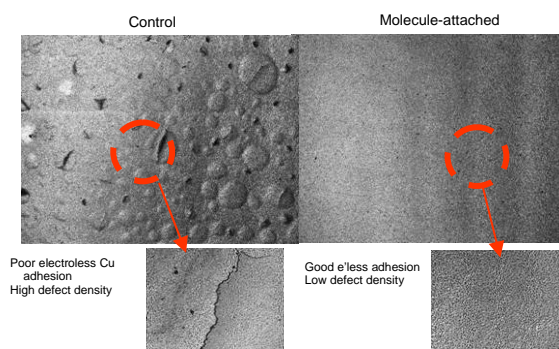

Figure 3: Process Summary

Figure 4: SEMs of Copper Surface on Control and Molecule-coated ABF-GX13 substrates.
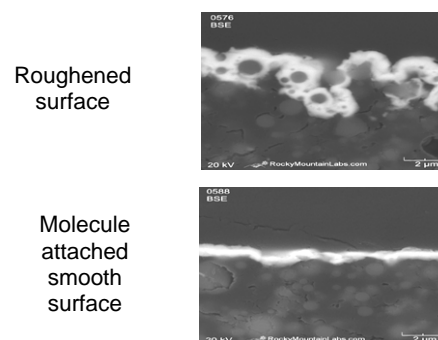

Figure 5. Cross-section SEM's of electroless Cu deposited on roughened and molecule-treated ABF-GX13 smooth surfaces.
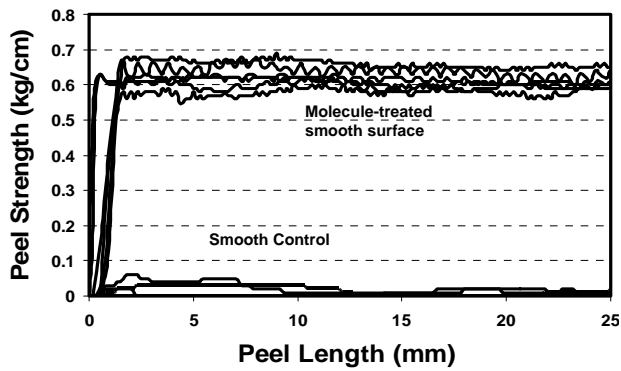
Figure 6. Copper peel strength of smooth and molecule-treated ABF-GX13 smooth surfaces.
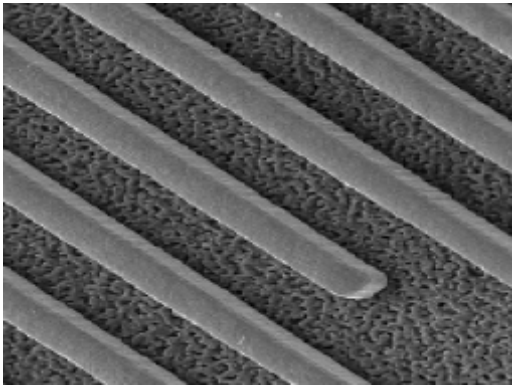

Figure 7. Example of fine-line patterned copper lines on molecule-treated smooth GX-13 substrate.

Table 1. Results of HAST tests on Molecule-treated, Smooth ABF-GX13 Substrates	
Test	**Result**
Peel strength	0.62 Kg/cm
Reflow and HAST	10% degradation vs. 13% for roughened control
Extended Bake	No degradation
Thermal Cycle	No degradation
Thermal Shock	4% degradation vs. 8% for roughened control
THS	9% degradation – same as roughened control

Table 2. Impact of Molecular Adhesion on Fine Line Patterning on ABF-GX13 Substrates		
Line/Space Dim. (um)	**Roughened Control Substrate**	**Smooth Molecular Substrate**
50/50 micron	Ra > 0.5 um, Features Defined	Ra ≤ 0.2 um, Features Defined
30/30 micron	Ra > 0.5 um, Features Defined	Ra ≤ 0.2 um, Features Defined
20/20 micron	Ra > 0.5 um, Features Defined	Ra ≤ 0.2 um, Features Defined
18/18 micron	Ra > 0.5 um, Some Defects & Delamination	Ra ≤ 0.2 um, All Features Defined
14/14 micron	Ra > 0.5 um, Significant Defects and Delamination	Ra ≤ 0.2 um, All Features Defined
8/8 micron	Ra > 0.5 um, Significant Defects and Delamination	Ra ≤ 0.2 um, All Features Defined

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