The Next generation of Multilayer Bonding of High-Performance Dielectric Materials in Compliance with lead-Free Initiatives

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Background

For component assembly onto bare printed circuit boards the electronics industry appears to be moving forward with the specification of Sn/Ag/Cu (SAC) alloys for lead-free processing. The liquidus temperature of the SAC alloys is in the range of 217 - 221 °C, compared to 183 °C for eutectic Sn/Pb solder. Depending on the thermal loading/complexity of the assembly, the profiling accuracy of the oven, and the alloy chosen, the peak re-flow temperature for SAC alloys is estimated to be 235 – 260 °C. At this conditions re-flow temperatures are likely to be even higher. Most lead-free qualification focuses around the effect of these higher temperatures on plated-through-holes i.e. interconnect stress testing, the final finish, electroless nickel, immersion gold, immersion silver, and lead-free solders as they relate to assemble. There is also a need for new substrates with higher glass-transition-temperature, and being halogen-free for a completely “Green” product. Higher soldering temperatures result in higher z-axis expansion, which will affect PTH reliability and inner-layer-bonding integrity. However, no work has been done on the effect of these higher assembly temperatures on the inner-layer bonding system.

In this paper the synergy of an Intergranular Etch (IGE) or Oxide Alternative with the white oxide will be examined. The synergy of these two systems yields a process that has all the advantages of both systems: High peel strength, excellent thermal reliability, no pink ring or wedge voids, and ease of horizontal processing, but none of their weaknesses.

Hybrid Process Description

Alkaline Cleaner

Developed primarily for aggressive cleaning applications for such residues as dry film resist and heavy fingerprints prior to Secure Etch process step.

Secure Initiator

Provides improved treatment in subsequent Secure Etch process step by providing protection of Secure Etch Bath against contaminates and providing the proper surface potential for the Secure Etch to etch.

Secure Etch

The Secure Etch is a modified sulfuric acid/hydrogen peroxide microetch that provides the surface topography by etching the copper crystals at their grain boundaries. This etching provides the necessary surface roughness for mechanical bonding. The resulting structures have high shear strength of copper metal rather than the low shear strength of copper oxide crystals.

Secure Enhancer

Consequently, the Secure Etched copper surface is coated with tin and subsequently laminated.

Test Vehicle

The primary test vehicles are a 6-layer and 12-layer printed circuit board treated with an Oxide Alternative bonding process. The panel contains 35 µm copper foil layers, constructed with various substrate materials. These panels were used for multiple reliability tests.

Test Methods and Responses

In this case several more intensive and quantifiable tests were done with peel strength being measured with each test lot for reference. After initial adhesion strength was measured samples were subject to multiple Lead-Free

Infrared Reflow cycles. After which the adhesion was measured again to determine the change in adhesion. It is believe that this data reflects what happens within the PCB during lead-free assembly.

Results:

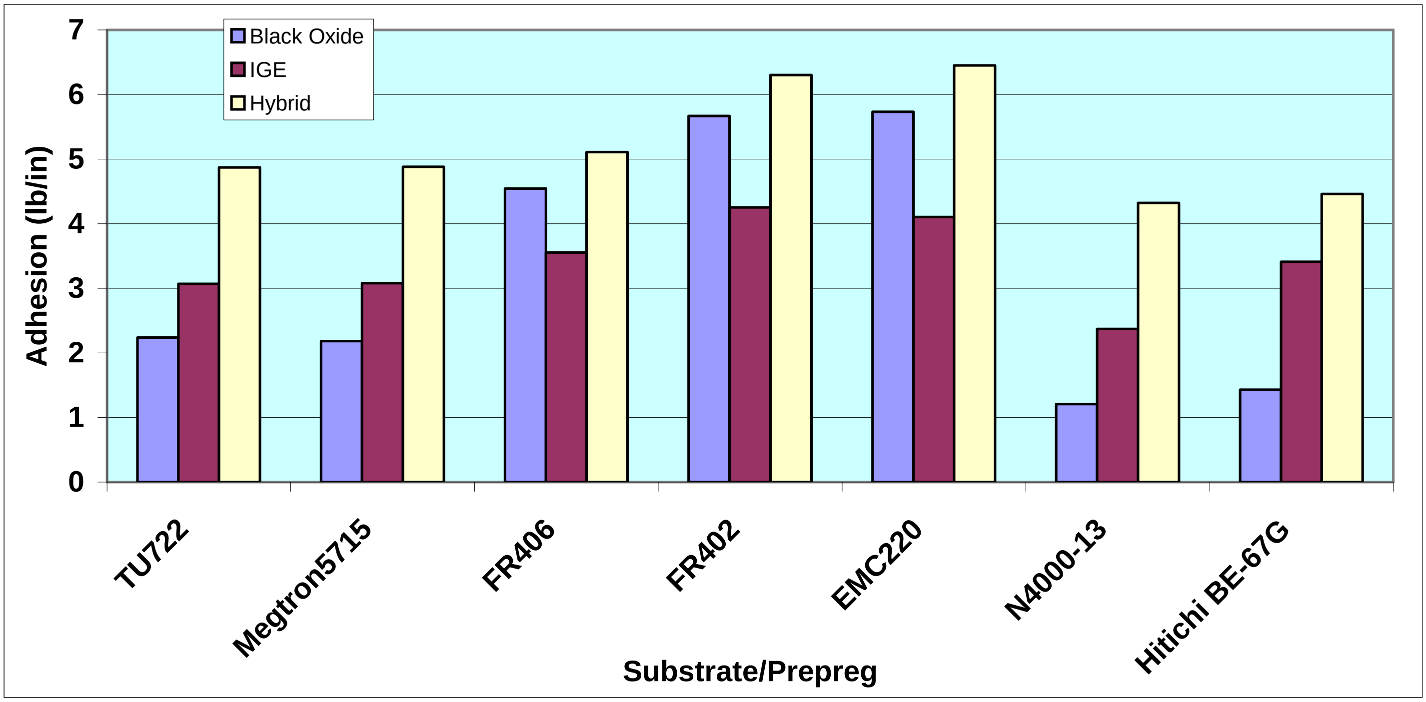

Chart 1. Adhesion (lb/in) by Substrate/Prepreg After Lamination

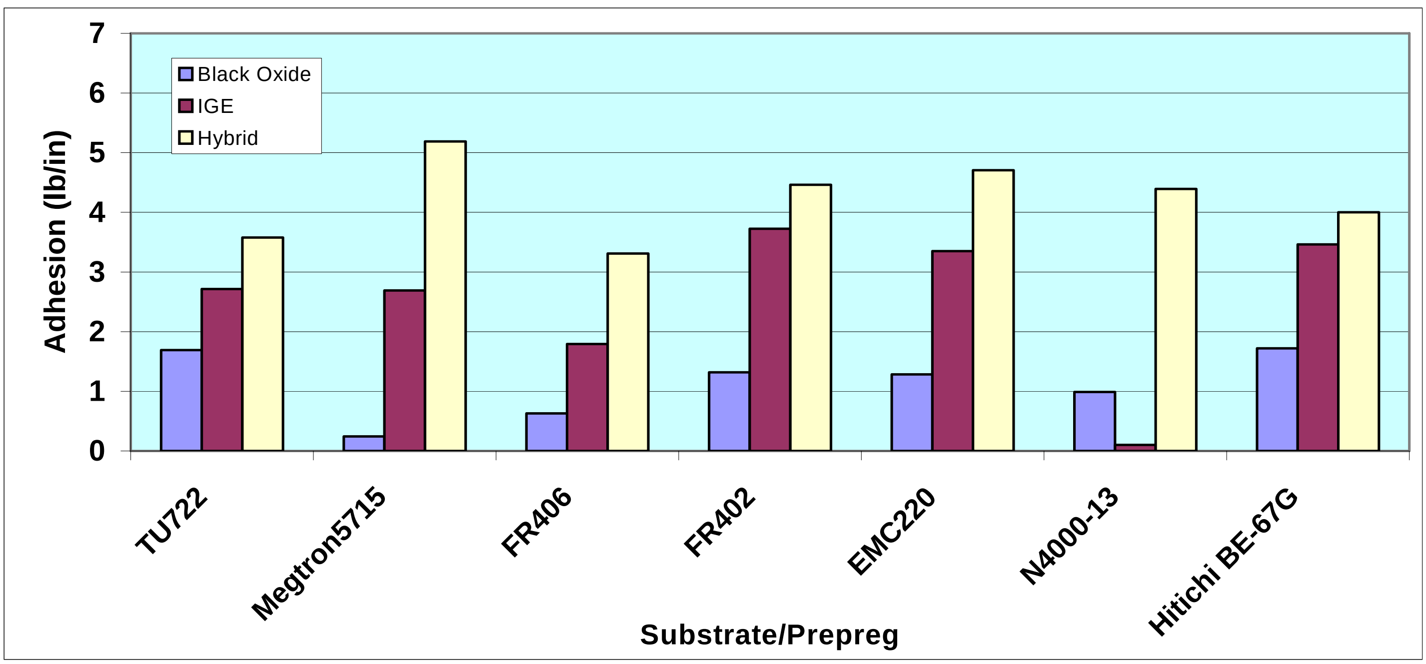

Chart 2. Adhesion (lb/in) by Substrate/Prepreg After 3 x Lead-Free Infrared Reflow

Also in compliance with lead-free solder initiatives samples were subject to a lead-Free re-flow profile then subjected to T-260 and T-288 testing. The lead-Free re-flow conditions chosen were that of "standard" lead-free thermal profile. After 10 cycles samples were then T-260 and T-288 Tested.

Material	Sample Layers	T260 (Minutes)	T288 (Minutes)
Hitachi	12 Layer	8.78	0.17
N4000-6		21.85	1.46
GETEK		36.46	4.46
FR408		> 40	5.62
FR402		6.13	0.00
Hitachi	6 Layer	8.52	0.39
N4000-6		3.36	0.00
GETEK		>40	7.53
FR408		>40	8.5
FR402		7.41	0.75

Table 1 Thermal Mechanical Analysis Results

DISCUSSION/CONCLUSION:

The Hybrid process has proven to be very robust. The DOE samples were processed while the Hybrid bath was at “steady-state” operation for standard production simulation.

The results are as expected. Black oxide displayed superior performance pre-Reflow for both standard FR4 as well as the Halogen free material. However, pre-thermal stress adhesion strengths are not what’s important but rather the adhesion after thermal stress. In this case, the superior adhesion of Black Oxide could not withstand multiple Pb-free Reflow cycles and suffers a loss of adhesion greater than 50%. Similarly the Alternative Oxide or IGE, the Alternative Oxide +Enhancer, and the Hybrid Oxide all experience adhesion loss. However, the Hybrid Oxides loss is minor in comparison to the other oxide coatings. The Hybrid suffers only a 6% loss in adhesion with the Halogen Free material compared to 28% and 54% losses with standard Alternative Oxide and Black Oxide respectively.

We also find the Hybrid process can withstand multiple Lead-free IR-Reflows using various substrates materials with more than acceptable T260 times. In the case of the T288 testing the primary failure was due to material failure. It would appear that perhaps the T288 test is not very reliable as a test method due to the extreme temperatures and subsequent prepreg breakdown.

This enhanced performance is due to the diffusion of tin with copper occurs to create an intermetallic film. The initial 0.25 µm layer of pure tin is completely transformed into an intermetallic film during the lamination cycle.

Heating causes micro structural changes in the copper/tin layer. The tin layer density decreases with time as the intermetallic layer grows and becomes thicker, while scattered micro void formation also occurs near the copper/tin boundary. All these results indicate tin diffusion into the copper layer. The growth of the intermetallic creates prolific fingerlike structures at the copper/intermetallic interface for enhanced mechanical bonding (figure1).

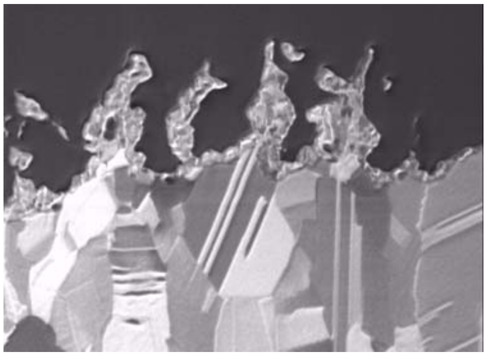

Figure 1. Intermetallic Growth at Interface

The chemical bond between metal and epoxy is more difficult to characterize, and many theories have been proposed over the years. It should be recognized that the surface of a copper circuit is composed of copper oxides, whether it has been treated with black oxide, reduced black oxide, or an oxide alternative. Unless the oxide surface is formed and kept in a vacuum, some of the copper oxides will hydrate when exposed to ambient humidity to form hydroxyl groups, and these hydroxyl groups interact with the epoxy in a weak acid-base reaction to form a chemical bond. The variation in adhesion strength observed with different metal oxide surfaces can be attributed to the surface charge, defined by the isoelectric point of the surface, or IEPS.

Using Halogen free or standard FR4 the Hybrid Oxide provides superior adhesion. The higher adhesion strength after lamination although reduced after multiple IR-Reflows, remains greater than 4 lb/in of adhesion. Thus, the Hybrid provides better process stability when attempting to meet the impending lead-free requirements of tomorrow.

Further study of Lead-Free soldering will be investigated at a later time. This testing will focus on isolation of the inner-layer-bonding systems i.e. samples without plated-though-hole for detail evaluation using T260 and T288 test methods.

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