High Performance Multilayer Bonding Systems

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Abstract

A new approach has been developed to address the reduced adhesion of the existing alternative oxide processes when used with advanced dielectrics. This process incorporates the processing advantages of modified sulfuric acid/peroxide intergranular etch with the improved adhesion properties of tin oxide. This paper describes the process parameters, adhesion properties with a variety of advanced dielectric materials.

Introduction

The trend in the PCB industry is toward high frequency applications. The major drivers are the producers of base stations, backplanes, wireless communications and high-speed computers. To successfully develop and employ the above-mentioned applications new and improved materials will be needed. Development of advanced resin systems will require low D_k, dielectric constants, and D_f, dissipation factors, as well as glass transition temperatures, T_g, of > 195 ^oC to ensure thermal and electrical reliability. Materials like polyimides, PI, polyphenylene oxides, PPO, Allylated polyphenylene ethers, A-PPE, cynate ether / epoxy blends, and expanded polytetrafluoroethylene, PTFE are already commercially available.

The market leader for inner-layer bonding of advanced materials has been reduced black oxide (Figure 1). Black oxide has long been an industry standard because of high peel strengths, appearance, and most importantly thermal reliability due to superior mechanical bonding.

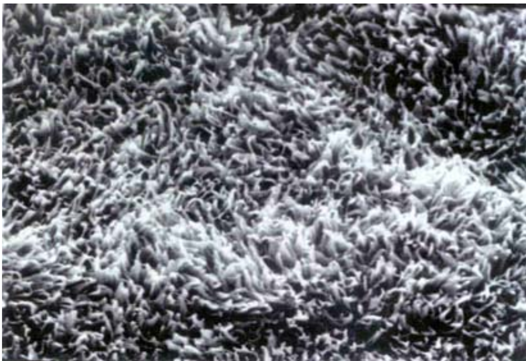

Figure 1. 10KX SEM of Black Oxide Surface

However, black oxide has many problems such as pink ring, wedge voids, easily fractured crystals when undergoing multiple lamination cycles, and hazardous processing conditions.

The earliest alternative oxide process was the white oxide process, which uses an alkaline cleaner, mono persulfate micro etch, immersion tin, and silane post treatment (Figure 2).

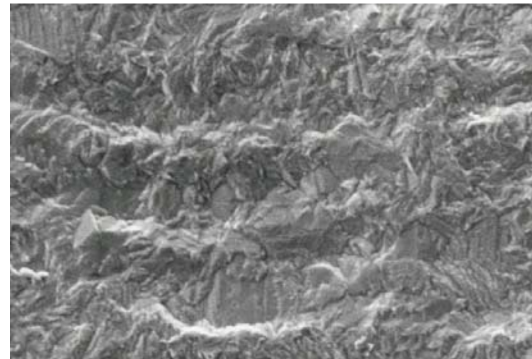

Figure 2. 5KX SEM of White Oxide Surface

Although this system has superior chemical bonding it obviously lacks the mechanical bonding, which leaves it incapable when resin systems do not form chemical bonds and are more reliant on mechanical adhesion.

Other oxide replacement systems were developed in the mid to late 90 s. They focused on horizontal processing using a simple three to four step processes, normally persulfate micro-etch, alkaline cleaner, activator, and an oxide replacement. These oxide replacements were generally modified sulfuric/peroxide micro etches or Intergranular Etch, IGE, that provided mechani-

cal and chemical bonding. They provided a microstructure that was very dense and low profiled (Figure 3).

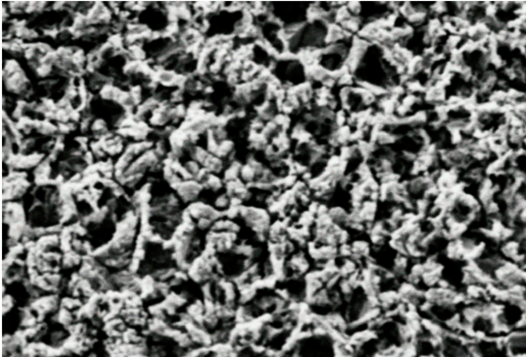

Figure 3. 5KX SEM Alternative Oxide Surface

These systems have many advantages over black oxide. The organometallic layer provides excellent protection against pink ring and wedge voids. The low profile structure also makes it more reliable in products requiring multiple lamination cycles, as it is not susceptible to fracturing. Replacement systems have not been able to achieve peel strengths equal to black oxide. However, they have proven comparable thermal reliability.

While each multilayer bonding system has its advantages as well as disadvantages none is the clear choice for processing advanced materials.

In this paper the synergy of an Intergranular Etch with the white oxide process will be examined. Lab scale and beta-site tests have shown that 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.

Experimental

There were three main effects that needed to be confirmed in the fusion of an IGE with white oxide.

1. The effects of surface topography, i.e. micro etch.
2. The effect of Tin Oxide
3. The effect of Silane

Table 1. DOE Variables & Parameters

Variable	Low	Mid	High
ME	Peroxide	Persulfate	IGE
Silane	Without	-----	With
Tin	Without	-----	With

The dielectric tested was GETEK™ a blend of Epoxy and Polyphenylene Oxides with a T_g of 185 ^oC.

Table 2. Test Matrix of Treatments

Foil	Micro Etch	Tin	Silane
1	Peroxide/Sulfuric	NO	NO
2	Peroxide/Sulfuric	NO	YES
3	Peroxide/Sulfuric	YES	NO
4	Peroxide/Sulfuric	YES	YES
5	Persulfate	NO	NO
6	Persulfate	NO	YES
7	Persulfate	YES	NO
8	Persulfate	YES	YES
9	Intergranular Etch	NO	NO
10	Intergranular Etch	NO	YES
11	Intergranular Etch	YES	NO
12	Intergranular Etch	YES	YES

Two foil samples were processed per test condition. The lamination "books" were constructed of C-stage material to provide rigidity, 2-ply of GETEK™, four 3"x6" copper foil samples, and one foil sample with the treated side down as a control. The resulting books were pressed using GETEK specifications in a lab scale press.

Table 3. Sample Processing Conditions in Horizontal Atotech Equipment

Process	Delivery	Time
Alkaline cleaner	Spray	30 s
Triple C/F Rinse	Spray	30 s
Activator	Flood	15 s
IGE	Flood	60 s
NaPS	Spray	60 s
Peroxide/Sulfuric	Spray	60 s
Triple C/F Rinse	Spray	30 s
Immersion Tin	Spray	45 s
Fresh Rinse	Spray	15 s
C/F Final Rinse	Spray	15 s
Air Dry	AFD	15 s
Silane Post-Treat	Spray	15 s
Hot Air Dry	AFD	30 s

Results/Discussion

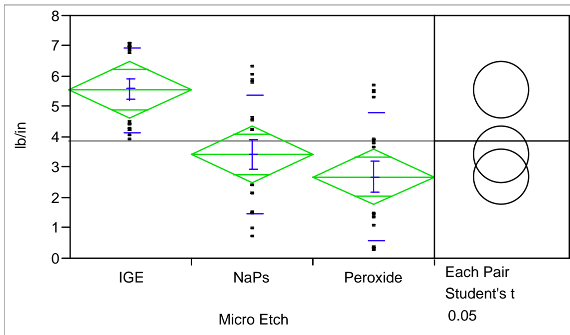

Figure 4. Effect of Micro Etch on Peel Strength

Table 4. Means and Std Deviations of Micro Etch Effect on Peel Strength

Level	Number	Mean	Std Dev
IGE	16	5.54086	1.38948
NaPs	16	3.41964	1.93304
Peroxide	16	2.69500	2.10001

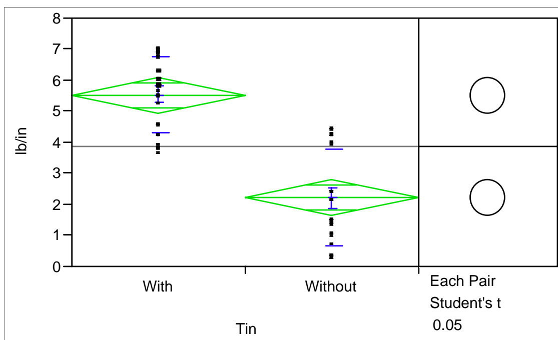

Figure 5. Effect of Tin on Peel Strength

Table 54. Means and Std Deviations of Tin Effect on Peel Strength

Level	Number	Mean	Std Dev
With	24	5.54252	1.21249
Without	24	2.22781	1.55328

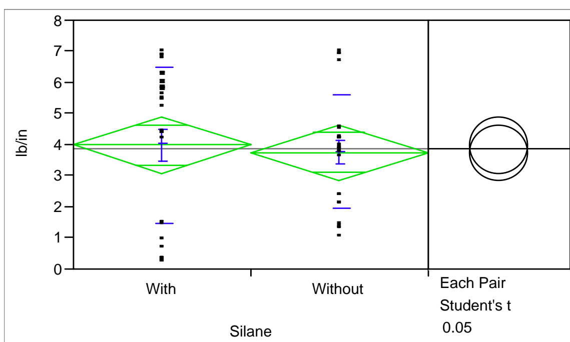

Figure 6. Effect of Silane on Peel Strength

Table 6. Means and Std Deviations of Silane Effect on Peel Strength

Level	Number	Mean	Std Dev
With	24	4.00367	2.51840
Without	24	3.76667	1.80102

Figures 4, 5, 6 and tables 4, 5, and 6 summarize the effects of each variable on the peel strength using GETEK Prepreg. Clearly the surface topography or Micro Etch, and the use of immersion tin are significant, while the presence of silane is not. However, this is not the entire case.

Silane is known for its ability to covalently bond with most resin systems and to strengthen the interfacial bond formed during the press cycle. However, it appears that the effect of the silane is inversely proportional to the surface topography of the copper surface. As the surface roughness increases (Table 7) the effect of the silane is reduced. By plotting the % increase of peel strength by adding silane to the tin surface the relationship can clearly be seen.

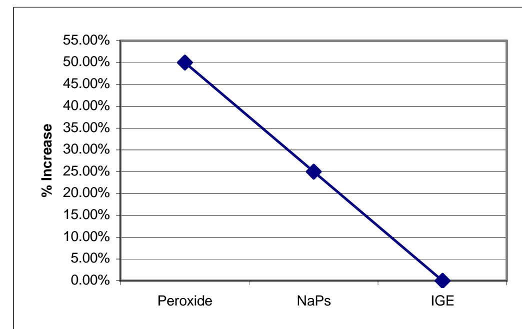

Figure 7. Inverse relationship of silane by surface topography

Therefore, silane is not necessary on an IGE surface morphology but does have a marginal effect on increasing peel strength.

Table 7. R_a Values of Surfaces

Surface	R_a
Peroxide	1000
NaPs	1800
IGE	2500

Stylus Profilometry

To further illustrate this point refer to Figures 2, 3 and 8 below for visual confirmation of surface topography.

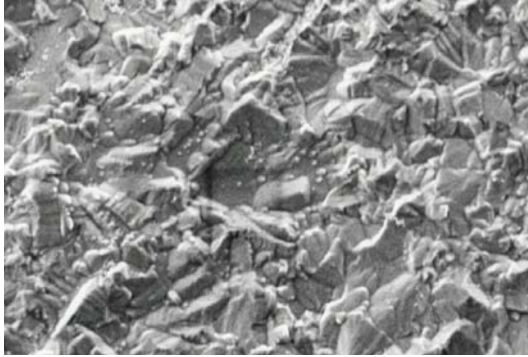

Figure 8. 5KX SEM of NaPS Surface

The factors which contributed to the high adhesion strength between epoxy and the IGE surface have both mechanical bonding and chemical bonding characteristics. These bonding mechanisms are best understood when compared to other surface treatments.

The mechanical bond between epoxy and a metal surface is affected by many factors, which are related to the epoxy, such as viscosity, wetting time, and surface tension. In addition, the surface topography of the metal can have a significant effect on the adhesion strength. The advantage of the IGE coating is that the topography of the copper surface is formed by etching pits into a rigid copper structure. The resulting structures have the high shear strength of copper metal rather than the low shear strength of copper oxide crystals.

Consequently, the intergranular etched copper surface was coated with tin (Figure 9) and subsequently laminated.

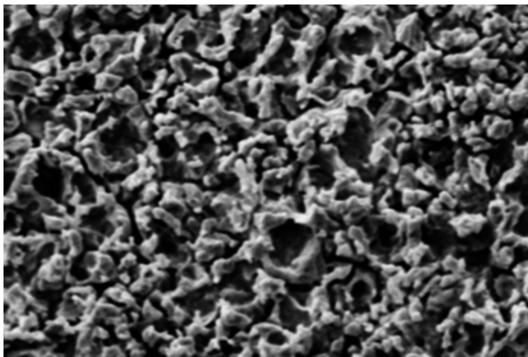

Figure 9. 5KX SEM of IGE Surface with Tin

During this heat cycle, 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 micro voids and fingerlike structures at the Cu/intermetallic interface for enhanced mechanical bonding.

The chemical bond between metal and epoxy is more difficult to characterize, and many theories have been proposed over the years[9]. 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 surface oxygen atoms 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, IEPS. Table 8 shows the IEPS values for several oxide surfaces.

Table 8. IEPS values for various metal oxides[9]

Oxide surface	IEPS	Oxide surface	IEPS
Ag^{+}	>12.0	Zn^{2+}	9.0
Mg^{2+}	12.2	Al^{3+}	9.1
Fe^{2+}	12.0	Fe^{3+}	8.5
Co^{2+}	11.3	Cr^{3+}	7.0
Ni^{2+}	11.0	Zr^{2+}	6.5
Pb^{2+}	10.3	Ti^{4+}	6.0
Cd^{2+}	10.3	***Sn^{4+}***	***4.5***
Be^{2+}	10.1	Mn^{3+}	4.2
Cu^{2+}	***9.1***	***Si^{4+}***	***2.2***

The interaction of the Metal Oxide IEPS values and adhesion strength to epoxy can be seen experimentally in Figure 8 below, as the IEPS value decrease the adhesion force increases.

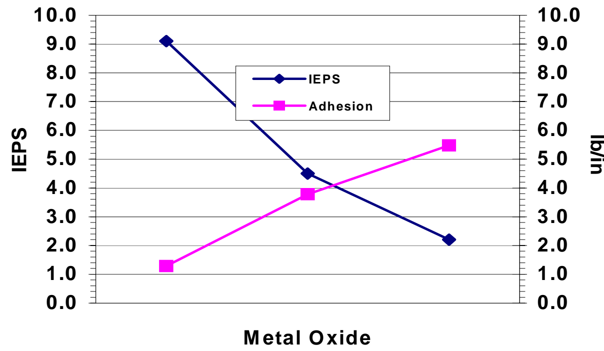

Figure 10. Plot of IEPS by Adhesion

Conclusion

The simple exchange of an Intergranular Etch for the mono persulfate microetch and the removal of the silane post-treatment has yielded a hybrid process with excellent potential for the future of multilayer bonding of advanced high T_g resins.

Table 9. Hybrid Process, Secure HTg

Process	Delivery	Time
Alkaline Cleaner	Spray	30 s
Triple C/F Rinse	Spray	30 s
Intergranular Etch	Flood	50 s
Triple C/F Rinse	Spray	30 s
Immersion Tin	Spray	45 s
Fresh Rinse	Spray	15 s
Triple C/F Rinse	Spray	30 s
Final Rinse	Spray	15 s
Hot Air Dry	AFD	30 s

These results are encouraging as we continue to see similar results with various High T_g resin system from a variety of vendors (Figure 11).

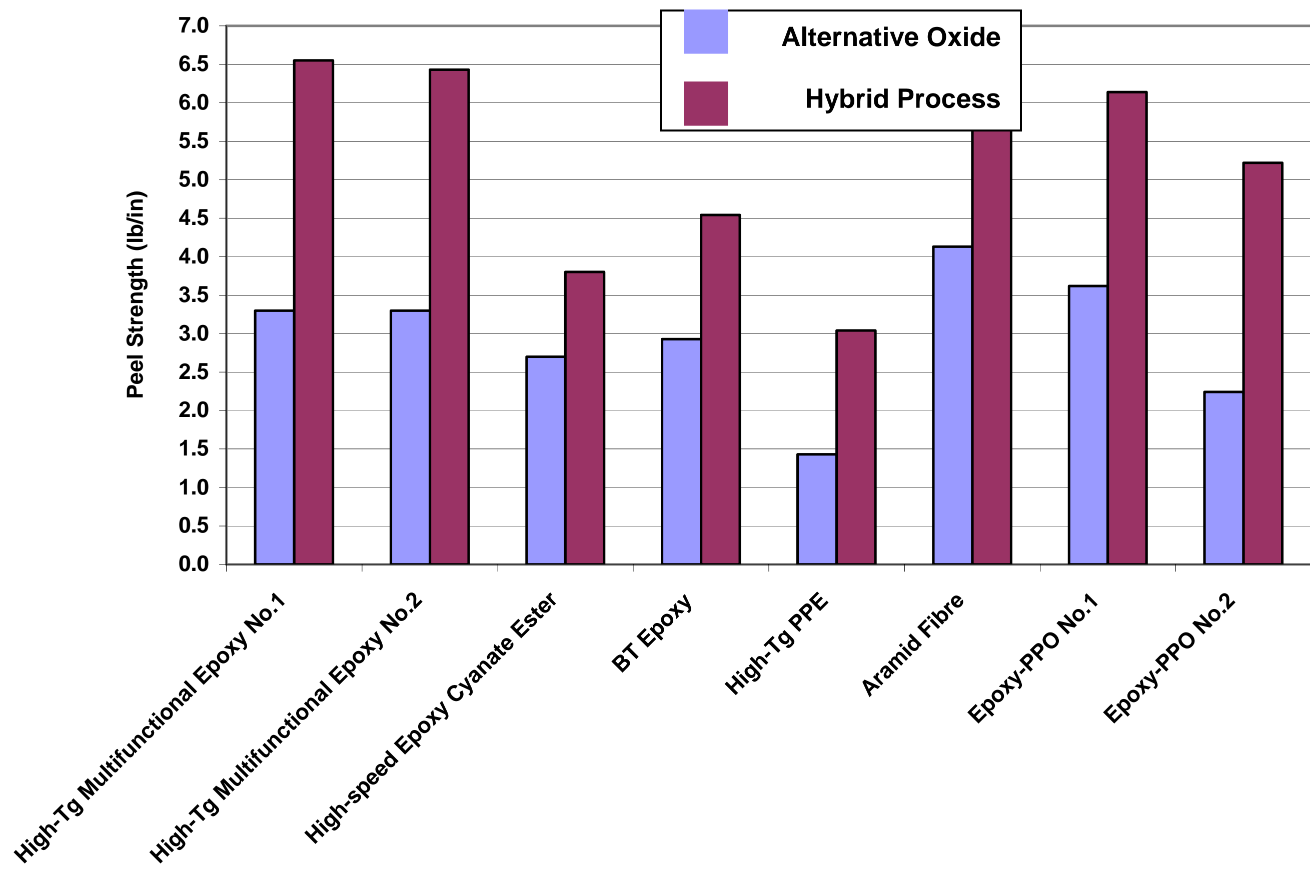

Figure 11. Peel Strength Comparison of Various Resin Systems

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