# Secure$^{TM}$ HT$_g$ – The Next generation of Multilayer Bonding of High-Performance Dielectric Materials in Compliance with lead-Free Initiatives

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## Abstract

Long-term continuing market growth within certain electronic sectors are fueling the need for new circuit board 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, $T_g$, greater than 195 $^oC$ to ensure thermal and electrical reliability. Materials such as polyimides (PI), polyphenylene oxides (PPO), allylated polyphenylene ethers (A-PPE), cyanate ester / 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.

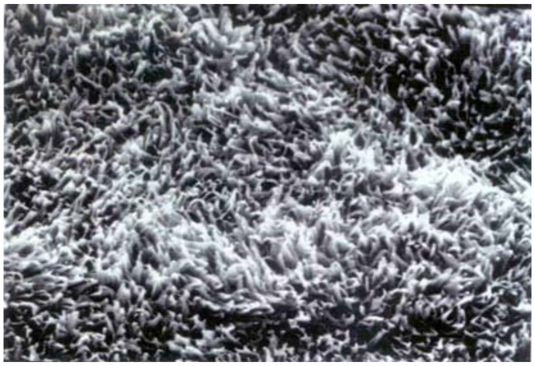

**Figure 1. 10KX SEM of Black Oxide Surface**

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 first commercially successful large-scale conveyorized multilayer bonding process was the “white oxide” process[1], which uses an alkaline cleaner, mono persulfate micro etch, immersion tin, and silane post treatment (Figure 2).

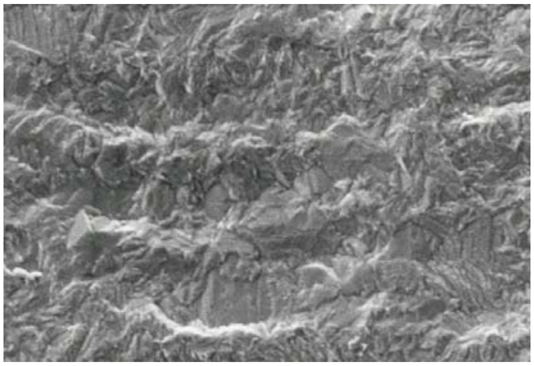

**Figure 2. 5KX SEM of White Oxide Surface**

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

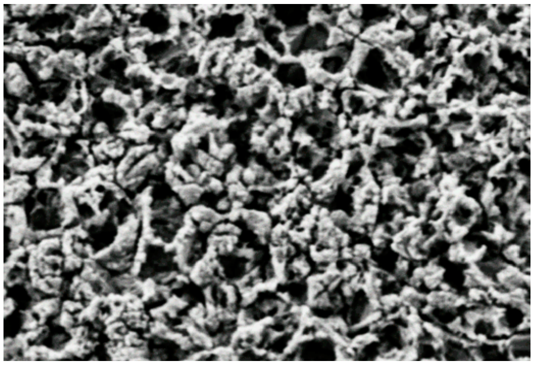

**Figure 3. 5KX SEM Alternative Oxide Surface**

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 combined 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 |
|---|---|---|---|
| M.E. | Peroxide | Persulfate | IGE |
| Silane | Without | ----- | With |
| Tin | Without | ----- | With |

The dielectric tested was GETEK$^{TM}$, a blend of epoxy and polyphenylene oxides with a $T_g$ of 185 °C.

**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 3x6-inch 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 and Discussion

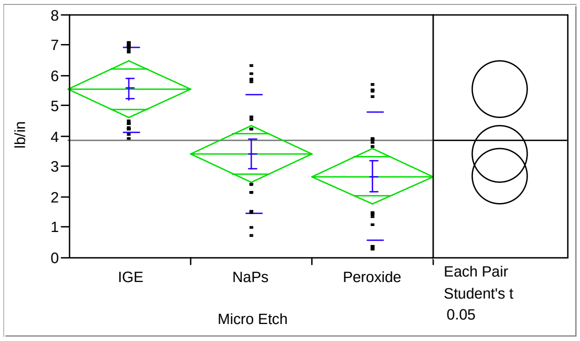

Figure 4. Effect of Micro Etch on Peel Strength

**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 |

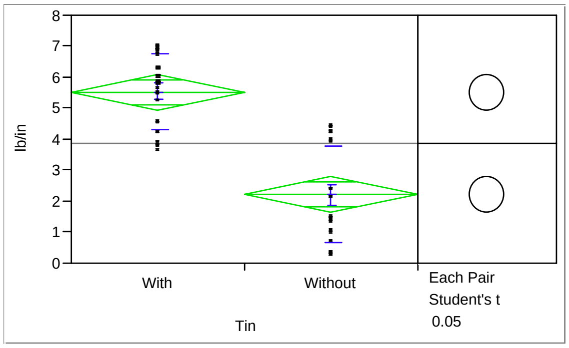

Figure 5. Effect of Tin on Peel Strength

**Table 5. 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 |

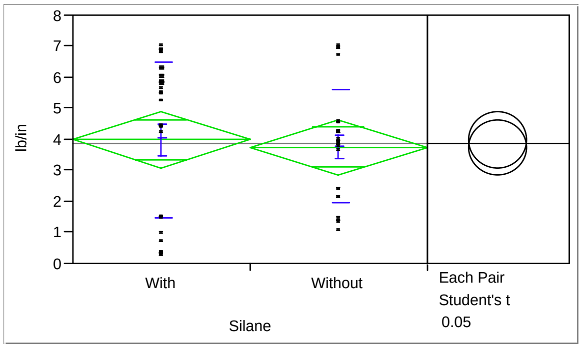

Figure 6. Effect of Silane on Peel Strength

**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 etches, 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 roughness 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 due to adding silane to the tin surface, the relationship can clearly be seen.

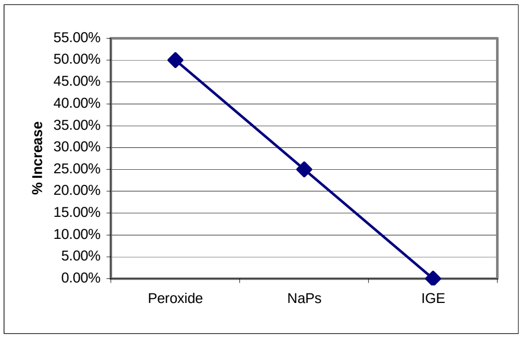

Figure 7. Inverse relationship of silane by surface topography

Therefore, silane is not necessary on an IGE surface morphology.

**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 3 and 8 below for visual confirmation of surface topography.

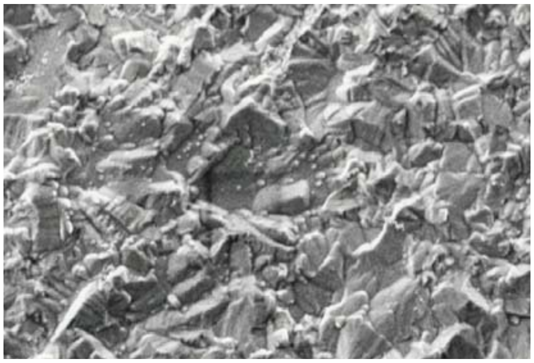

**Figure 8. 5KX SEM of NaPS Surface**

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 is coated with tin (Figure 9) and subsequently laminated.

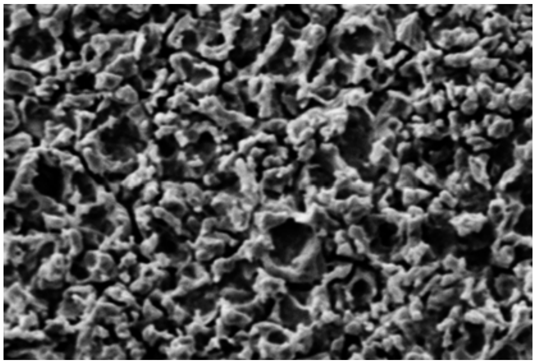

**Figure 9. 5KX SEM of IGE Surface with Tin**

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 copper / intermetallic interface[3] 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[2]. 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[2]**

| 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 10. As the IEPS value decreases, the adhesion force increases.

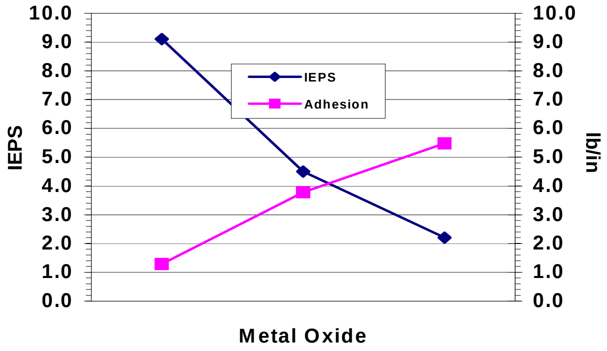

Figure 10. Plot of IEPS by Adhesion

## Conclusion

The simple exchange of an intergranular etch for the mono persulfate micro-etch 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 indicative of the higher bonding performance that can be achieved with various High $T_g$ resin systems from a variety of vendors (Figure 11).

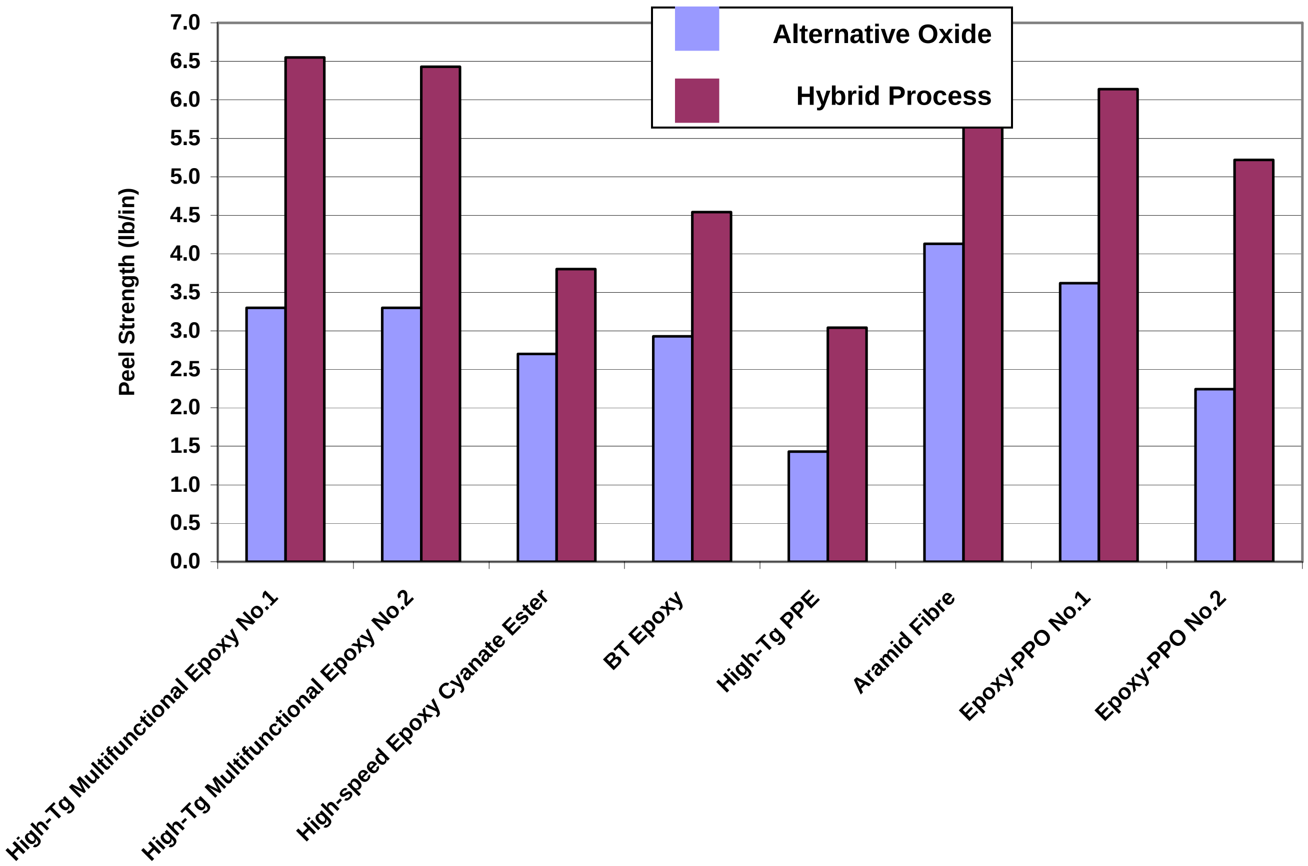

Figure 11. Peel Strength Comparison of Various Resin Systems

## References

1. Applied Technology Report Multi-layer Bonding: Current technology and a New Alternative; K.H. Dietz, J.V. Palladino, A.C. Vitale; Dupont Electronics; February 1991

2. J.C. Bolger and A.S. Michaels, “Interface Conversion for Polymer Coatings,” P. Weiss and D. Cheever, Editors, Chapter 1, Elsevier, New York, 1968.

3. Investigation of Phase Growth in the Copper-Tin System; S. Däbritz, V. Hoffmann, G. Sadowski, D. Bergner; Defects and Diffusion Forum Vols. 194-199 (2001) pp. 1575-1580