Building STRONG Bonds

By **Michael Carano, Lee Burger, Al Kucera and Roger Bernards**

Enhancing interlaminar bond strength for high performance resin systems with an organo-metallic copper surface treatment process.

With continued emphasis on long-term reliability and vastly improved electrical performance, manufacturers of high layer count multilayer PWBs are beginning to abandon the reduced oxide bonding process in favor of alternative methods. One such method, described by the authors as an organo-metallic adhesion promotion system, increases the bond strength of the resin to the copper by modifying the topography of the copper surface and simultaneously depositing an organic layer that acts as an adhesion promoter. The surface area or topography of the copper is enhanced by the selective microetching along the grain boundaries of the copper. This organo-metallic process is used because higher performance resins and other advanced materials require higher pressures and temperatures for lamination. With reduced oxides, the needle-like structures composed of cupric oxide are very fragile. Typically, these higher pressures and temperatures cause these needles to fracture, reducing bond strengths. The structure of the oxide is shown in Figure 1 below.

Contrast this with the structure shown in Figure 2. Here, one can see that the actual grain structure is formed by the selective micro etching along the grain boundaries of the copper. One can't see (from this SEM) the organic coating that is co-deposited on the surface However, analysis of the surface with various analytical techniques will reveal the presence of an organic material. The structure of the copper is one of copper metal, not a copper oxide crystal. The organic coating functions as a covalent bond enhancer with the functional resin system.

Theory of Bonding and Process Description

There are two main factors involved in enhancing the bonding strength of copper to the pre-preg for multilayer lamination of circuit boards: the type and degree of roughness imparted to the

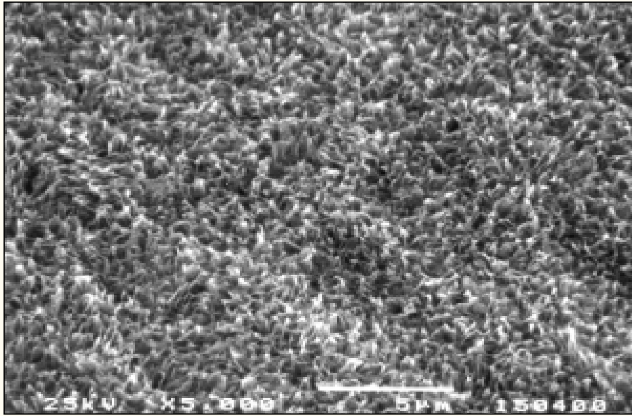


Figure 1. SEM view of reduced oxide coating.

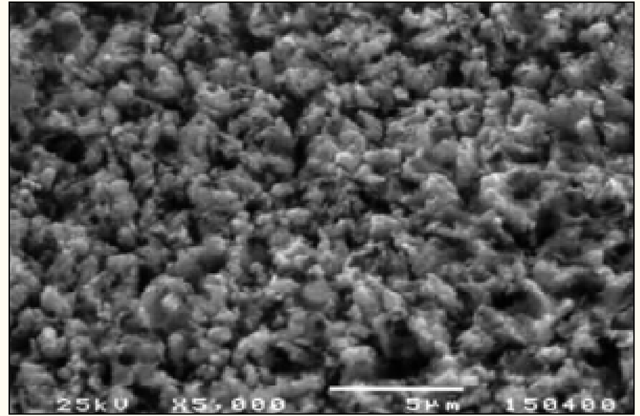


Figure 2. SEM view of the structure of the organo-metallic copper crystal structure.

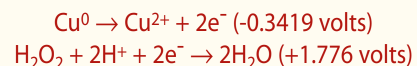
copper surface, and the type and thickness of any coating applied to the copper surface (1).

Roughness. Current oxide coating processes impart micro-roughness to the copper surface that greatly exceeds the degree of roughness that is obtained with normal copper micro-etchants. In order to match or exceed the bond strength that oxide processes impart to the copper, these micro-etchants would need to be reformulated to greatly increase the degree of roughness (4). Not all forms of roughness are the same. For example, sanding the copper surface would impart a great deal of roughness to the surface but the bonding strength would still be very low due to the fact that this roughness would be macro-roughness rather than micro-roughness. Good copper adhesion starts with imparting a micro-roughened surface to the copper. This roughness can only be seen with a SEM at powers of about 2000X or higher. A power of 5000X is commonly used. With such a photograph of the surface we see that a typical oxide process roughens the copper on the order of 0.1 to 0.5 microns peak to peak. Also, the peak to valley distance (perpendicular to the copper plane) is greater than the peak-to-peak distance (parallel to the copper plane). The type of micro-roughness (different peak-to-peak and peak-to-valley distances) will influence the bonding characteristics of the copper to the pre-preg. Even shape (prism-like, jagged, round, bent, etc.) can influence the bonding characteristics (1).

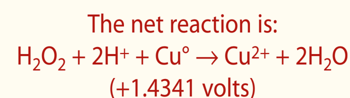
Different pre-pregs will have different flow and wetting characteristics. It is possible that some pre-pregs will flow and wet out the entire micro-roughened surface from top to bottom. While other pre-pregs with low flow characteristics may not be able to flow all the way down to the bottom of the valley and may not completely wet out the micro-roughened copper. This leaves a micro-gap at the bottom of the valley where solution can leach into the coating and cause issues, maybe even pink ring (even though the peel strengths are high). So it is conceivable that some pre-pregs will like a certain type of micro-roughness, and other pre-pregs may do better with another type of micro-roughness (2).

Coatings. Current oxide processes also forms a coating on the copper surface that exhibits different chemical and physical properties. For example, the wettability of the oxide surface is different than an equally roughened bare copper surface. The ability of the pre-preg to chemically and physically adhere to the surface is dependent on what that surface is, in addition to its surface area. The coating thickness and strength of the overall coating play a major role. For example, a very long oxide needle is fragile. Thus, an oxide coating that is too thick does not give good peel strengths even though the surface is very rough. The alternative process (organo-metallic) imparts a coating on the copper surface at the same time as etching/micro-roughening the surface. Unlike the inorganic oxide coating, the alternative coating is organic (often referred to as an organo-metallic). During the oxidation of the copper, a metal/organic coordinate is formed that is insoluble in the process solution. This coating is a vital part of the bonding mechanism. Tests have shown that copper surfaces with equal or even greater degree of micro-roughening, but which do not contain a metal/organic coating, do not provide good bonding characteristics, especially with respect to time to delamination. The organo-metallic coating increases the bond strength, especially at high temperature stress conditions such as solder immersion. This is due to chemical interaction between the copper and the coating, (a coordination bond is formed), and the coating and the pre-preg (a sharing of pi electrons occurs) (1).

Chemical Reaction. Organic metallic process is a peroxide-sulfuric based etching and coating solution that has been specially and uniquely formulated to impart micro-roughness to the copper surface that greatly exceeds normal etchants and at the same time forms a coating on the surface that promotes adhesion through chemical bonding. Peroxide etches copper by oxidizing Cu^0 to Cu^{2+}. The half-cell reactions are shown below:

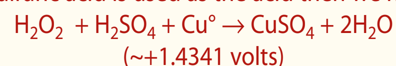


$$Cu^0 \rightarrow Cu^{2+} + 2e^- \ (-0.3419 \text{ volts})$$
$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \ (+1.776 \text{ volts})$$



The net reaction is:

$$H_2O_2 + 2H^+ + Cu^\circ \rightarrow Cu^{2+} + 2H_2O$$
$$(+1.4341 \text{ volts})$$



If sulfuric acid is used as the acid then we have:

$$H_2O_2 + H_2SO_4 + Cu^\circ \rightarrow CuSO_4 + 2H_2O$$
$$(\sim+1.4341 \text{ volts})$$

This reaction consumes one mole of peroxide, one mole of sulfuric acid and one mole of copper metal and produces one mole of copper sulfate and two moles of water. The positive voltage indicates that this reaction is spontaneous and the rela-

tively high voltage of this chemical system further indicates that virtually every molecular collision of peroxide with copper will result in a reaction (when the acid is in excess). This means that the number of collisions per second controls the reaction rate. So the higher the peroxide concentration, agitation, and temperature, the faster the reaction will go. The reaction above indicates that there is no gas produced by the reaction, yet when boards are etched with peroxide one can visually see gassing at the board surface. This means that the reaction is not 100% efficient and that some peroxide reacts at the surface by spontaneously breaking down.

$$H_2O_2 \rightarrow H2O + \frac{1}{2} O_2 \uparrow$$

Any mixture of peroxide and acid will etch copper. However, most printed circuit board applications use proprietary formulations in which special additives are added to this system to impart a better, more stable, and predictable etching solution. These additives do not directly partake in the etching reaction but act as catalysts to alter the reaction rate or change the type of roughening produced by the etch (discussed below). In the case of alternative process, an organic coating is deposited. Also, since peroxide is fairly unstable, stabilizers that inhibit the spontaneous decomposition of peroxide are a necessary ingredient in the formulation.

Function of Topography Modifier and Adhesion Promoter

The organo-metallic chemistry is function specific because it contains proprietary additives that adsorb onto the copper surface which influence the etch rate on a sub-micron scale. This causes the imparted roughness to be several times greater than without these additives. The additive adsorption on the surface causes the etch rate at the copper grain boundaries to be increased greatly over the etch rate away from these grain boundaries. This causes the resulting surface roughness to be much greater than a normal peroxide/sulfuric etchant. This type of influence on the etch rate is called topography modification. The additive is organic in nature. In addition to topography modification, the additive coordinates the copper ions as oxidation is occurring. This is a special, Cu^{1+}/organic coordinate that is insoluble in the solution and coats the surface. This special coordination only occurs when an additional additive is present which acts as a catalyst to the reaction. This catalyst for the Cu^{1+}/organic coating reaction is an additional additive that acts as a coating promoter. This coating is known to promote bonding to the pre-preg. For lack of a better term, one can refer to this as an adhesion promoter. The promoter causes the oxidation of copper to occur in two steps. With a standard peroxide etch, the copper metal oxidizes from Cu° to Cu^{2+} in one step. That is, there is no relaxation step in the activation barrier of going from Cu° to Cu^{2+}. However, with the promoter present, the copper oxidation follows a two-step mechanism, Cu° to Cu^{1+} to Cu^{2+}. There is a dip in the activation barrier at Cu^{1+}. This two-step mechanism only occurs within certain concentration ranges of the promoter molecule. Outside these ranges (both low and high) the mechanism reverts back to a one step oxidation. With the two step oxidation mechanism, the modifier is able to form an insoluble coordinate with the Cu^{1+} specie before it oxidizes to Cu^{2+}. The promoter thus creates an intermediate step. As stated earlier, the Cu^{1+}/organic coordinate is insoluble and coats the surface. Also, oxidation can continue. The Cu^{1+}/organic coordinate can be further oxidized to Cu^{2+} and organic. The organic is then free to search for more Cu^{1+} coming from the new surfaces being created by the etch. (1) The topography modification/organic coating mechanism is depicted in Figure 3.

Because the coating is formed during the etching of the copper surface, the coating has to fight for the surface as the surface itself is being etched away. The coating is dynamic in that as oxidation continues, the existing coating (the copper/organic coordinate) is dissolved and a new coating (with the freshly oxidized copper) is formed, replacing the old. The organic that was bound to the copper surface goes back into solution and seeks out new copper being oxidized and reforms the coating. Therefore, since the coating is constantly being destroyed and recreated, it is a dynamic coating. In this way only a relatively thin coating thickness can be accomplished. The coating thickness cannot build up indefinitely, but will be limited to a relatively thin layer. It is beneficial to avoid excessive coating thickness. [Note: Similar to oxide where a lower weight gain provides an improved bond over the thicker, heavier oxide coatings] (3).

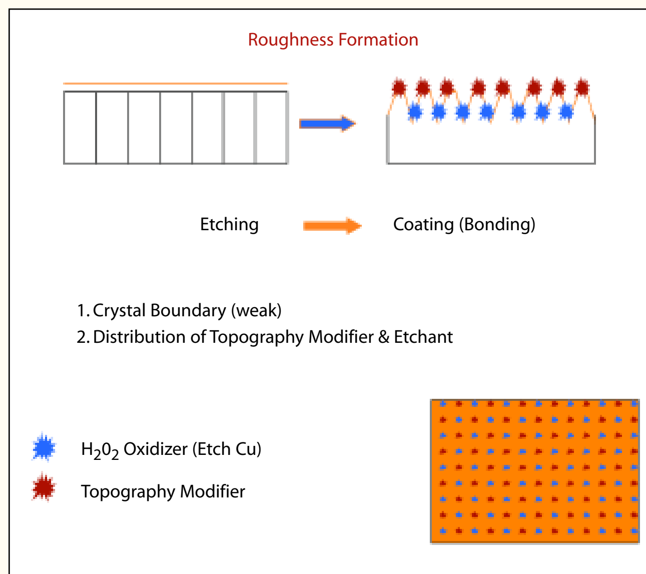


Figure 3. Theory of roughness formation.

The promoter also contains additives which help to maintain even adsorption of the topography modifier.

The physical characteristics of the substrate are more important in the organo-metallic bonding process than in the reduced oxide process. There is a good reason for this. In the reduced oxide process a crystal of copper oxide is additively “grown” from the surface. This growth process is referred to as anodic oxidation of copper in an alkaline medium. The roughness seen on the SEM photo in Figure 1 is from this crystal growth. The copper oxide in the crystal is a product of copper metal being oxidized in an alkaline medium. These copper oxide crystals are loosely held and somewhat fragile.

In the organo-metallic process, the roughness seen on the

SEM photo in Figure 2 is the substrate. The organo-metallic process subtractively "etches" the substrate. The roughness imparted into the substrate is a direct function of the grain structure of the substrate. These differences in the substrate characteristics manifest themselves as different thickness of the organo-metallic coating deposited on the substrate and in different degrees of roughness.

Key process parameters including acid concentration, organic additives concentrations (both the topography modifier and adhesion promoter) are the critical performance indicators for bond strength. Coating thickness/uniformity and the etch topography/profile are closely controlled by maintaining the proper concentration ranges for the sulfuric acid, topography modifier and adhesion promoter.

In the Figures 4-7, test panels made of FR-4 (140 Tg and 170 Tg) material) on one ounce copper were tested for peel strength to measure the bond integrity under various operating conditions. The performance ratings (1-10) indicate a rating schedule whereby the higher the number, the better the overall bond integrity. The performance rating scores were determined from a composite of recognized test methods including peel strength, solder shock, pink ring resistance and pressure cooker testing.

The above figures details the effect on the bond strength versus the amount of copper removed. It is obvious that with thin foils, the amount of copper removal be minimized without compromising bond strength.

Bond Strength to Prepreg

The original premise to the process design was that the alternative technology has to provide optimum reliability in terms of bond strength for high performance resin and advanced materials. Typically, this included materials with Tg of 170°C and above, as well as polyimide, FR-5 and GETEK®.

Peel strength testing data was supplemented with pressure cooker testing, thermal stress and time to delamination. An interesting upside to the alternative oxide process was overall improved reliability with the higher performance resin systems. This was attributed to the combination of a micro-roughened surface and an organic adhesion promoter that enhanced the resin adhesion for the higher Tg materials. Reduced oxide coatings, consisting of needle-like copper oxide crystals, easily fracture during the higher temperatures and pressure required during lamination (5).

The following chart (Figure 8) show the peel strength data. To determine peel strength, standard HTE copper foils (1 ounce) were processed in the organo-metallic process and additional foils processed through reduced oxide as the control. The treated foils were laminated with the various resins under recommended parameters from the suppliers. The prepreg style chosen in each case was one sheet of 7628 and one sheet of 1080. The lighter weight was always laid up against the treated foil.

Standard peel strengths were performed per IPC-TM-650 2.4.8 C condition A. The results are listed in Figure 8 for one

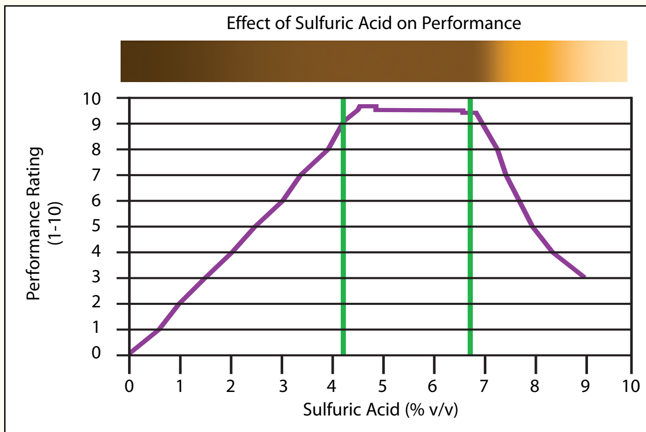


Figure 4. Effect of sulfuric acid concentration on performance.

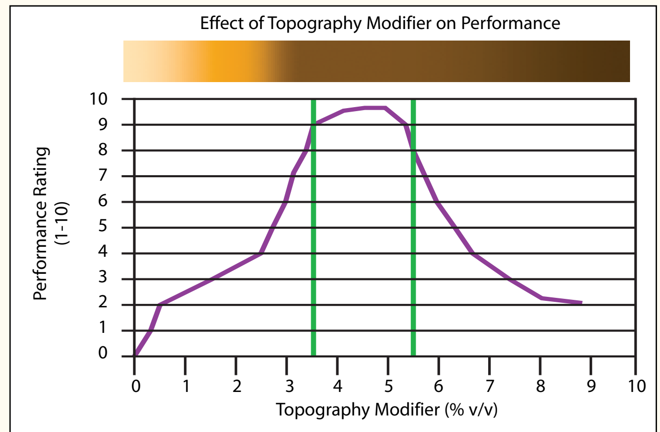


Figure 5. SEM view of the structure of the organo-metallic copper crystal structure.

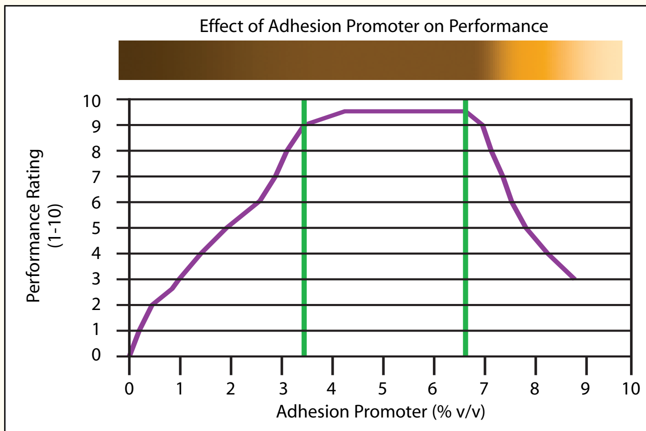


Figure 6. Effect of adhesion promoter on performance.

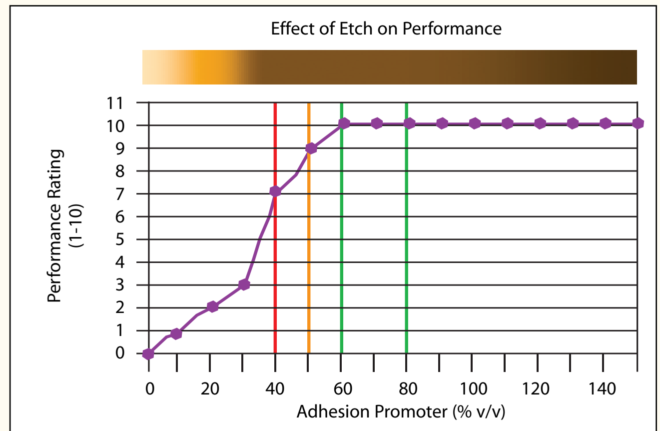


Figure 7. Effect of copper etch amount on performance.

materials supplier. One interesting fact about the organo-metallic bonding process was that the peel strengths achieved on higher performance materials generally were higher than the standard oxide processes. The increased interlaminar bond strength was attributed to not only a mechanical bond additionally a chemical adhesion mechanism to the organo-metallic coating.

Bonding strength not withstanding, the multilayer PWBs fabricated with the organo-metallic bonding process must meet stringent performance requirements. The T-260 testing-time to delamination was already acknowledged as to its importance in qualifying alternative bonding processes. Other reliability metrics include IPC accredited methods including thermal stress, pressure cooker and pink ring resistance.

Thermal stress requires floating multilayer coupons on molten solder at 288°C for 10 seconds, and repeating for nine more cycles. There shall be no evidence of delamination.

The pressure cooker test (IPC-TM-650, method 2.6.16) is designed to measure the ability of the package to withstand a highly accelerated temperature and humidity stress test. No delamination can occur under the conditions of 30 minute dwell, at 15 psi pressure cook, followed by a 10 second float on molten solder. Solder temperature to be 2600°C.

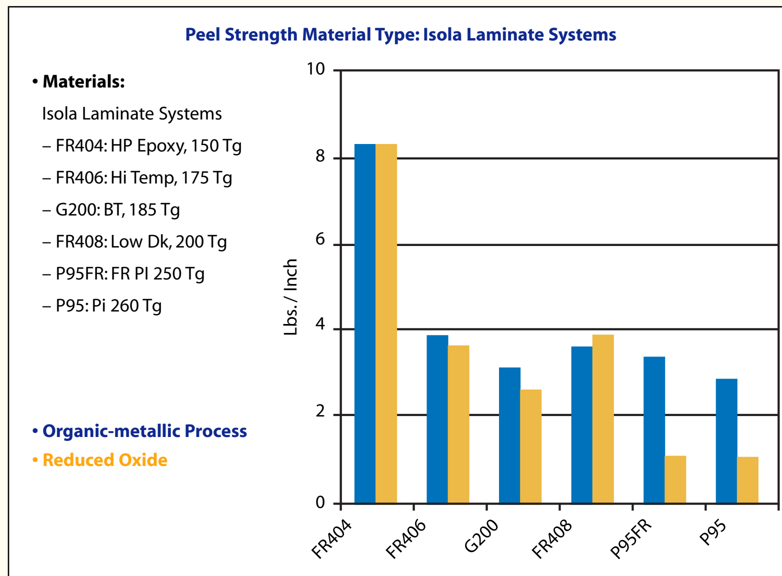


Figure 8. Comparison of peel strengths for various resin systems with organo-metallic vs. reduced oxide.

Process Control

The organo-metallic bonding process offers advantages over standard oxide processes in terms of consistency and ease of control. Replenishment of the organo-metallic bonding solution is usually done with a "feed and bleed" system. Typically components are pre-mixed in a side tank and then replenished based upon a panel counter, a copper sensor or a specific gravity controller.

Each of the control methods has its advantages and disadvantages. A panel counter is easy to use and involves little maintenance but it does not accurately track copper build up in the bath when panel size and % copper area vary widely. A copper sensor measures copper concentration by determining the amount of light that can pass through the solution. Due to the organo-metallic complex that is formed the etching solution may foul the light sensor resulting in the need for more frequent maintenance of the probe. The specific gravity controller measures the specific gravity of the solution, which is influenced by all of the components as well as copper concentration. If the bath components are controlled within a consistent range then specific gravity is a good indicator of copper concentration. If the bath components, especially sulfuric acid, are not controlled within the proper limits, then the specific gravity controller will not accurately control copper concentration. Despite the drawbacks of the control methods all three of the methods have been used successfully in field applications.

As an added benefit the concentration of all major components of the alternative bonding bath can be analyzed using simple analytical procedures. This minimizes performance problems by ensuring the bath components are properly balanced. Proper balance of the components is necessary so that appearance, bond strength and resistance to thermal excursions are all acceptable. This is especially critical when using high performance resin systems such as high Tg FR-4, polyimide and PPO.

Summary

The organo-metallic adhesion promotion system offers many benefits to the fabricator. By improving the speed at which the coating is formed on copper surfaces, productivity in the interlayer fabrication area has increased several fold. The process speed and the relative simplicity of this technology (as compared to reduced oxide) allows for easy adaptation to either vertical (immersion) or horizontal conveyorized modes. Capital spending outlays to implement the process is significantly less than reduced oxide, and return on invested capital can be realized in a matter of months.

Productivity gains aside, the most important aspects of any technology are its process capability and the long-term reliability of products fabricated with the process. The organic metallic process described herein details the metrics employed to measure process capability and reliability. There are many more applications for the organo-metallic process. These applications, including primary imaging and sequential build, will be the topic of future articles. **CT**

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Michael Carano, Lee Burger, Al Kucera and Roger Bernards are all employed by Electrochemicals (Maple Plain, MN). For more information, email mcarano@electrochemicals.com.

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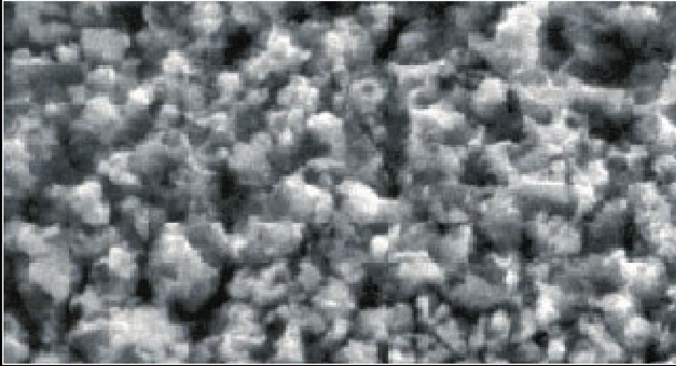

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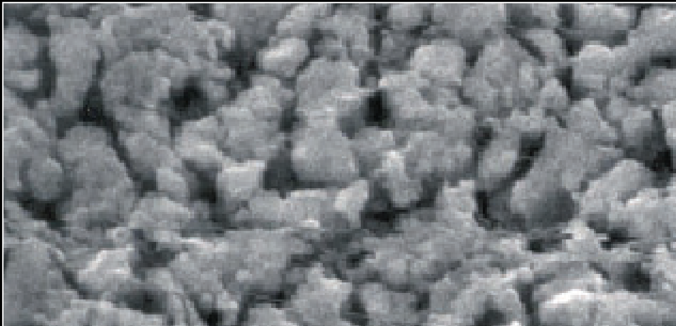
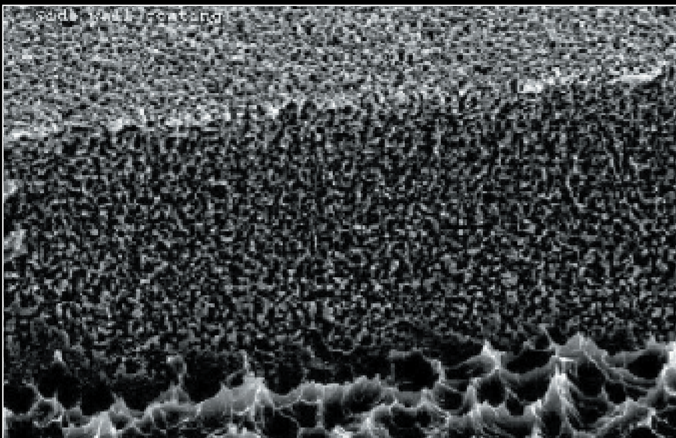


Conventional oxide alternative - 30 microinch removal of copper - note poor topography.



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