

Semi-Additive Process for Low Loss Build-Up Material in High Frequency Signal Transmission Substrates

Fei Peng¹, Naomi Ando², Roger Bernards¹, Bill Decesare¹

¹ MacDermid Enthone Electronics Solutions, Waterbury, CT, USA

² MacDermid Enthone Electronics Solutions, Hiratsuka City, Kanagawa, Japan

Abstract

Higher functionality, higher performance and higher reliability with smaller real estate are the mantras of any electronic device and the future guarantees more of the same. In order to achieve the requirements of these devices, designs must incorporate fine line and via pitch while maintain good circuitry adhesion at a smooth plating-resin interface to improve signal integrity. The Semi-Additive Process (SAP) is a production-proven method used on low dielectric loss tangent (Df) build-up materials that enables the manufacture of ultra-fine circuitry.

The standard SAP process utilizes some roughening or texturing of the dielectric substrate in order to achieve sufficient adhesion; however, the rough surface at the plating-resin interface potentially increases transmission loss at high signal speeds. To promote signal integrity at high-frequency signal transmission, the next SAP process should provide high plating-resin adhesion as well as very smooth interface in between.

The next build-up material in demand should present high thermal and dimension stability, good chemical resistance to survive many cure and reflow processes in circuitry manufacture. It should also deliver excellent electric properties including high insulation reliability, low Df and low dielectric constant (Dk) to guarantee good signal integrity in high frequency signal transmission. Meanwhile, the good properties above bring challenges to the SAP process.

This paper will discuss a new SAP process for low loss build-up materials with low desmear roughness (Ra= 40-100 nm) and excellent adhesion (610-680 gf/cm) at various processing conditions. Along with the process flow, the current work will also present results and a discussion regarding characterization on the morphology and composition of resin and/or metal plating surfaces using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), surface roughness analysis, plating-resin adhesion evaluation from 90° peel tests.

1. Introduction

New electronic devices are getting more functional but smaller, which continuously pushes technology to new levels. This miniaturization trend demands ultra-fine circuitry, which incorporates laser drilled blind microvias, tighter pitch, finer lines and spacing. At the same time, it requires high speed signal transmission with high signal integrity. Semi-Additive Processing (SAP) has been widely used in the manufacture of ultra-fine circuitry on different dielectric build-up materials.

Good candidates for dielectric build up materials should provide good process-ability as well as excellent chemical resistance; good dimension stability (i.e. low constant of thermal expansion) and sufficient mechanical strength. These outstanding properties make circuitry manufacture possible by eliminating smear and warpage through multiple chemical treatment, cure and reflow processes involved. Moreover, they ensure good circuitry integrity and guarantee long-term reliability of electronic devices used at a wide range of temperatures. In addition, the potential candidates should have excellent electrical properties, including low dielectric loss tangent (Df) and low dielectric constant (Dk), which are essential for high speed signal transmission.

In order to decrease signal loss and increase signal integrity at a high transmission speed, the surface of dielectric materials should be maintained as very smooth while the adhesion between them and fine circuitry should be excellent; however, the standard SAP process dramatically roughens dielectric surface to seek sufficient adhesion through an anchor effect. The

next SAP process should use very mild surface texturing but add significant chemical functioning to provide high plating-dielectric adhesion at very smooth interface in between.

Our company developed a new SAP-RIGID process for low loss build-up materials with low desmear roughness ($R_a=80\pm 18$ nm) and excellent adhesion (658 ± 18 gf/cm) at various processing conditions. Along with the process flow, the current work will also present results and a discussion regarding characterization of the morphology and composition of resin and/or metal plating surfaces using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), surface roughness analysis, plating-resin adhesion evaluation from 90° peel tests.

2. New Semi-Additive Process Flow

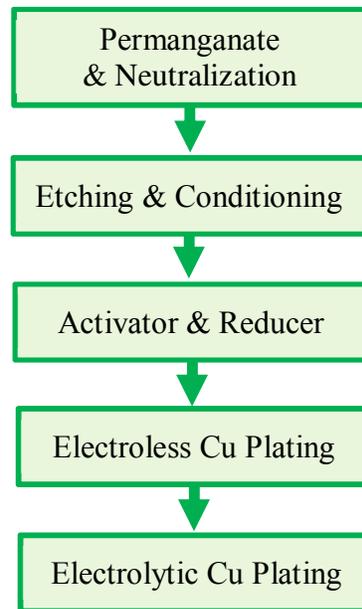


Figure 1. SAP-RIGID process flow.

The process flow for SAP-RIGID is listed in Figure 1. Generally, it includes similar steps as in traditional SAP, which makes it adaptable to existing equipment sets. In detail, the SAP-RIGID process combines metallization techniques tailored for rigid dielectric materials from our company, including surface pretreatments before plating (including permanganate and neutralization, etching and conditioning, activation and reducer), electroless and electrolytic plating techniques. In the pretreatment steps, the dielectric material is imparted with a very smooth but highly functionalized surface. After activating and reducing, a thin Cu seed layer with a thickness adjustable from 0.25 to 1.00 μm (i.e. 10-40 μin) was applied on the dielectric surface using an electroless Cu plating process. This Cu layer provides the film surface with good electrical conductivity which results in a uniform electrolytic copper thickness across the panel width. In the last step, electrolytic Cu plating was used to build up Cu thickness to the idea value. The influence of each processing step was demonstrated and discussed as follows.

3. Results and Discussions

3.1. Surface Pretreatment

In SAP-RIGID, surface pretreatment starts with a 12-25 min permanganate process at 80°C , which generates abundant carboxylate functional groups on the dielectric surface while just roughens it slightly. After that there is a neutralization step followed by a conditioning step in a caustic solution. This short time (5-10 min) etching and conditioning step can be done at a wide temperature range from 50 - 70°C . This surface pretreatment flow is much milder compared to traditional SAP for rigid dielectric materials, which normally starts with a strong sweller. The sweller step is normally operated at high caustic content, high temperature for 20-30 min, which is eliminated in the SAP-RIGID flow.

As a result, after the surface pretreatment in SAP-RIGID, the roughness on an epoxy and/or cyanate ester type dielectric surface is still as low as $R_a=80\pm 18$ nm, compared to that of raw dielectric material at $R_a=50\pm 5$ nm as received. The

dielectric surface before and after pretreatment are also compared underneath SEM, whose images are presented in Figures 2. Compared to the raw dielectric surface, there are obviously more dents rather than sphere-like bumps on the treated dielectric surface. These dents are homogeneously distributed and were formed due to release of some glass fillers from the surface after treatment.

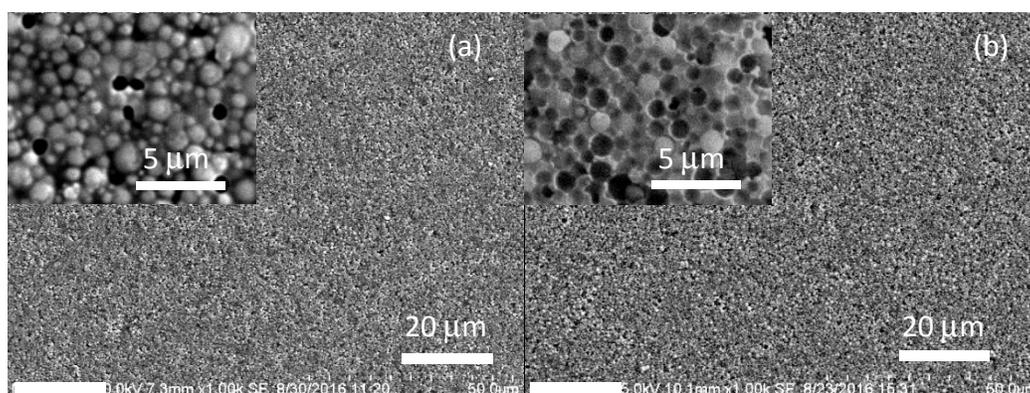


Figure 2. SEM images for the dielectric material (MATERIAL A) before (a) and after (b) SAP-RIGID pretreatment at 1000× magnification. Inserted are some of their surface enlarged at 5000× magnification respectively.

Such changes on the topography of the pretreated dielectric is accompanied with modification on its surface chemistry, which can be reflected from the atomic ratio on dielectric surface. As shown in Table 1, the EDX results demonstrate that the C/Si atomic ratio on pretreated dielectric surface increased to 3.3 ± 0.0 from that of 2.7 ± 0.1 on the raw one ($p < 0.001$). Moreover, the O/(C+Si) atomic ratio on pretreated dielectric surface increased to 0.66 ± 0.01 from 0.56 ± 0.02 ($p < 0.001$). Considering the two sets of comparisons, it can be concluded that the surface pretreatment in SAP-RIGID significantly introduced functional groups with carbon at higher oxidation stage. Furthermore, the chemical groups on pretreated and raw dielectric surfaces were also investigated using ATR-FTIR spectroscopy (Spectra are not shown here). A new big bump-like absorption from $3100\text{--}3600\text{ cm}^{-1}$, which is well-known as --OH stretching band region including hydrogen bond, was found on pretreated dielectric surface. It further proves that abundant carboxyl functional groups were successfully introduced to the dielectric surface after the pretreatment.

Table 1. EDX for atomic composition on dielectric surface before and after surface pretreatment in SAP-RIGID, separately.

| Dielectric Surface | Element | atomic% | C/Si, atomic | O/(C+Si), atomic |
|---------------------|---------|---------|--------------|------------------|
| Before Pretreatment | C | 47.8 | 2.7 ± 0.1 | 0.56 ± 0.02 |
| | O | 35.0 | | |
| | Si | 17.2 | | |
| After Pretreatment | C | 46.2 | 3.3 ± 0.0 | 0.66 ± 0.01 |
| | O | 39.6 | | |
| | Si | 14.2 | | |

3.2. Electroless Cu Plating

Following surface pretreatment, ionic activator and reducer are used to seed the dielectric surface with palladium. Then direct metallization processes are utilized to build up dielectric-metal laminate. In detail, an electroless Cu plating is applied to obtain a thin Cu seed layer. This electroless Cu bath is operated around $27\text{--}35\text{ }^{\circ}\text{C}$ and the plating rate in it can be tailored from 0.4 to $1\text{ }\mu\text{m}/\text{min}$ by adjusting plating temperature and additive contents. Figure 3 shows the SEM images for the morphology of electroless Cu layers generated at $0.75\text{ }\mu\text{m}/\text{min}$ with a thickness around $20\text{ }\mu\text{m}$.

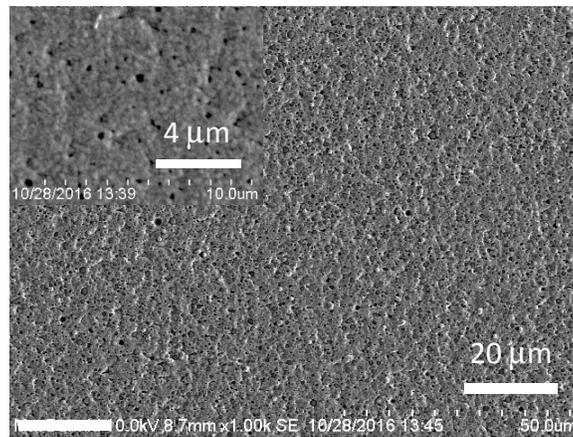


Figure 3. SEM image (1000× magnification; inserted, 5000× magnification) for electroless Cu layers plated on pre-treated MATERIAL A at 0.75 μin/min with a thickness around 20 μin.

3.3. Electrolytic Cu Plating

With the new SAP-RIGID technology, an electrolytic Cu plating process was used to build up Cu thickness. Figure 4-(a) exhibits the topography of electrolytic Cu plating on the dielectric material. By adjusting current density and plating time, the Cu thickness could be tailored to the ideal value with preferred plating rate, which proved to show little influence on dielectric-plating adhesion using SAP-RIGID.

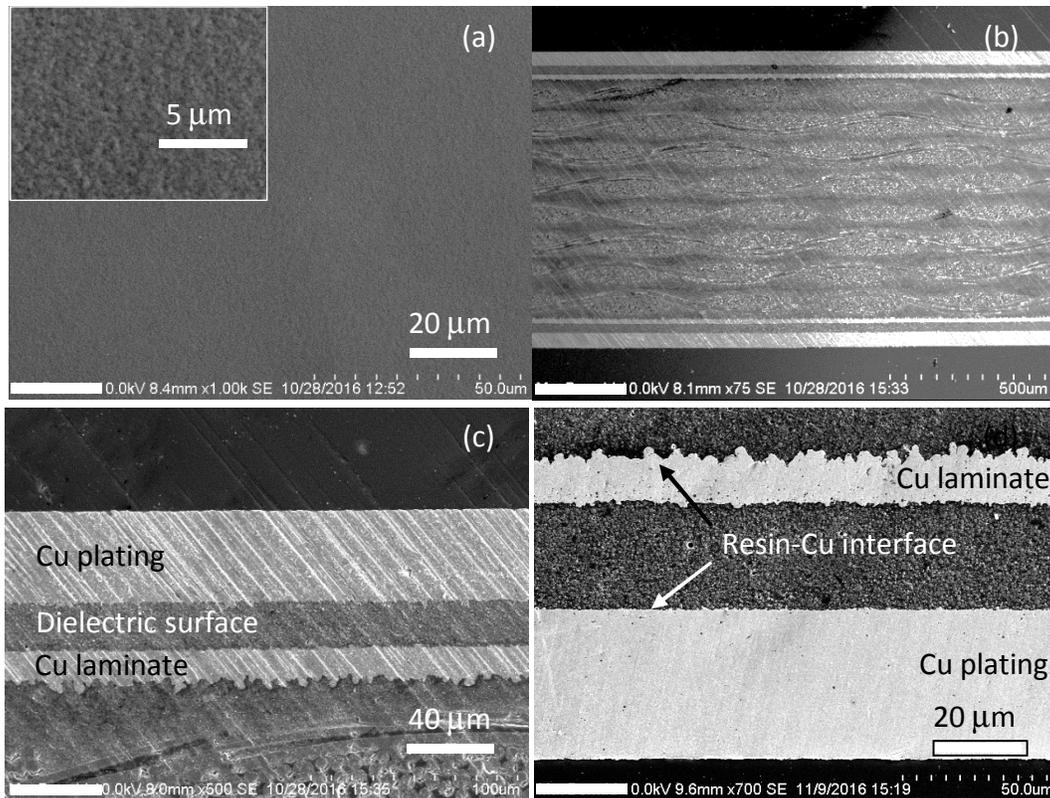


Figure 4. (a) SEM images (1000× magnification; inserted, 5000× magnification) for final electrolytic Cu layers on MATERIAL A. (b) SEM images showing cross-section of MATERIAL A with electrolytic Cu plating on both surfaces. (c-d) SEM images showing enlarged areas at the cross-section.

Figure 4-(b-c) show cross-section images of the plated dielectric laminate. Apparently, electrolytic plating generated uniform Cu plating layers on both sides of the SAP-RIGID processed dielectric board. In Figure 4-(c, d), special attention should be focused on the Resin-Cu interface. The interface between the inner Cu laminate layer and resin layer shows many

Cu feet providing bonding between the Cu laminate and inner resin layer through an anchor effect, which is similar to traditional metallization methods. On the contrary, the interface generated with SAP-RIGID process between dielectric surface and Cu plating is much smoother with no Cu foot.

3.4. Dielectric-Plating Adhesion

The adhesion between the treated dielectric surface and plating was evaluated by the bond strength at dielectric-plating interface by a 90° peel test. Freshly processed with SAP-RIGID, plated dielectric samples were cut into 1 2.54 cm × 5.72 cm L specimens and tested. Figure 5 shows a representative load versus dislocation profile from a 90° peel test on MATERIAL A processed with SAP-RIGID. It is evident that the dielectric-plating adhesion is uniform and averaged at 670 gf/cm through the testing length regardless of the edge effect at the end of the specimen.

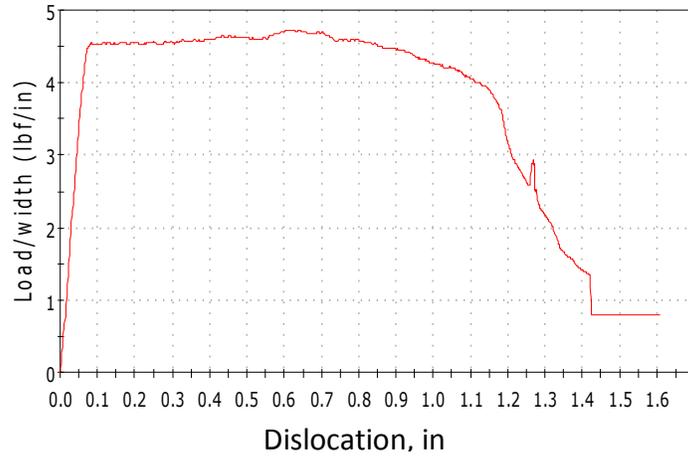


Figure 5. Representative load versus dislocation profile from 90° peel tests showing dielectric-plating adhesion processed with SAP-RIGID on MATERIAL A with electrolytic Cu plating around 20 μm.

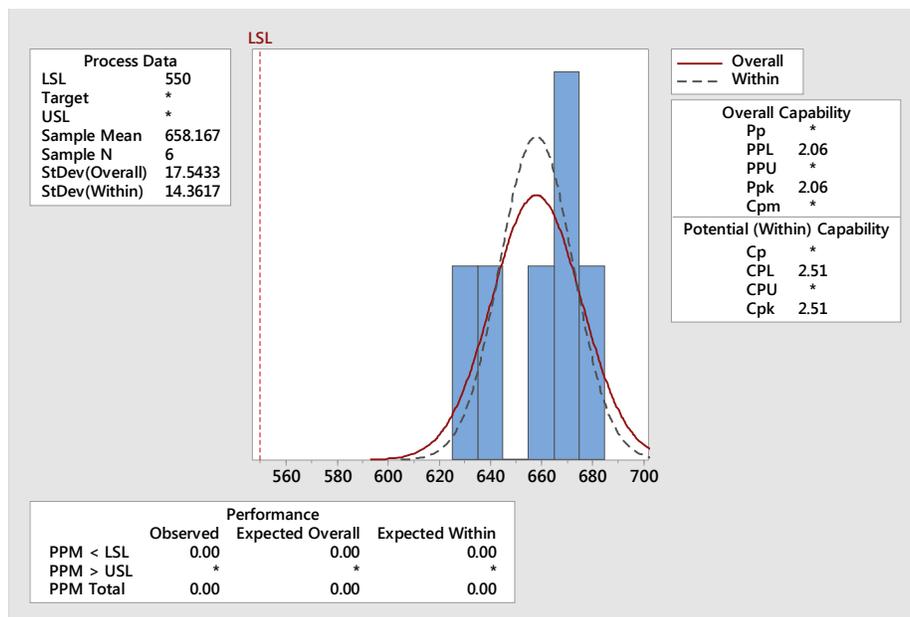


Figure 6. Statistical analysis of dielectric-plating adhesion and capacity evaluation of SAP-RIGID process on MATERIAL A with electrolytic Cu plating around 20 μm.

In order to evaluate the repeatability and consistency of the adhesion, more replicate experiments were performed by processing MATERIAL A using the SAP-RIGID process. At the same time, the capacity of the SAP-RIGID process was evaluated based on the adhesion results. As demonstrated in Figure 6, using the SAP-RIGID process, the dielectric-plating

adhesion averages 658 ± 18 gf/cm. Compared to a general adhesion lower limit for the adhesion on MATERIAL A, which is 550 gf/cm, the SAP-RIGID process has a short-term capability at 2.51 and a long-term capability of 2.06. In other words, our SAP-RIGID process is a typical 6-sigma capable process, which can consistently and continuously deliver satisfactory adhesion.

3.5. Preliminary Application on other Dielectric Materials

In addition to investigation on MATERIAL A, some preliminary studies were also carried out by applying the new SAP-RIGID technique on other rigid dielectric materials (MATERIAL B, MATERIAL C, MATERIAL D and MATERIAL E). The surface morphology of these dielectric materials after SAP-RIGID pretreatment are shown in Figure 7, respectively.

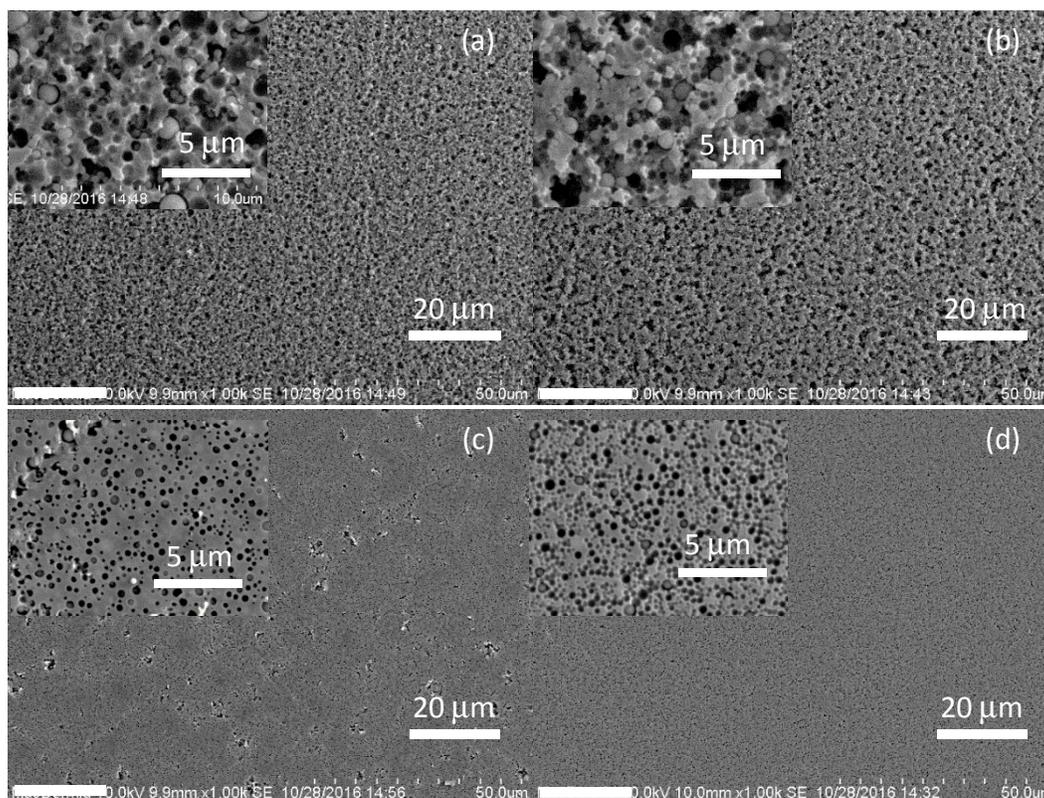


Figure 7. SEM images (1000× magnification; inserted, 5000× magnification) for different dielectric surface after pretreatment in SAP-RIGID: (a) MATERIAL B, (b) MATERIAL C, (c) MATERIAL D, and (d) MATERIAL E, respectively.

Due to their various chemical and physical properties, MATERIAL B, MATERIAL C, MATERIAL D and MATERIAL E responded differently to the current SAP-RIGID pretreatment. Some gained a rougher surface like MATERIAL B and MATERIAL C, while some maintained very smooth surface like MATERIAL D and MATERIAL E. And their adhesion data are summarized in Table 2. Apparently, processed with current SAP-RIGID, the four dielectric materials obtained various bonding to the Cu plating, which cannot be simply explained by the surface roughness. For example, MATERIAL E showed very low surface roughness down to 19 nm but sufficient adhesion. These results prove well that the good dielectric-plating adhesion from SAP-RIGID is based on chemical bonding rather than an anchor effect.

As is well known, a chemical bonding based SAP process should be developed with chemical and thermal treatments tailored regarding the surface composition, surface chemistry and T_g of the polymer phase on the top layer of each dielectric material. As shown in Table 2, the new SAP-RIGID process has good potential to be applied to more dielectric materials with minor adjustment on chemistry and fine tuning on processing parameters.

Table 2. Plating-dielectric adhesion on different dielectric materials.

| Dielectric materials | Ra after pretreatment, nm | Dielectric-plating adhesion, gf/cm |
|-----------------------------|----------------------------------|---|
| MATERIAL A | 80 | 670 |
| MATERIAL B | 215 | 393 |
| MATERIAL C | 131 | 520 |
| MATERIAL D | 27 | 529 |
| MATERIAL E | 19 | 409 |

4. Conclusions

The new SAP-RIGID process combines innovative etching, conditioning and direct metallization techniques from our company. It contains similar processes as traditional SAP, which makes it adaptable to existing equipment sets. Moreover, the processed dielectric surface can maintain low surface roughness as well as supports superior dielectric-plating adhesion through chemical bonding. The SAP-RIGID process has been successfully applied to an epoxy and/or cyanate ester type dielectric materials MATERIAL A and achieved very low desmear roughness ($Ra= 80\pm 18$ nm) and excellent adhesion (658 ± 18 gf/cm) on it. Considering the general lower limit for the dielectric-plating adhesion on MATERIAL A (550 gf/cm), the application of the current SAP-RIGID is a typical 6-sigma capable process both in short-term ($Cpk= 2.51$) and long-term ($Ppk= 2.06$). In addition, SAP-RIGID also opens good potential on other dielectric materials widely used in the current SAP market.