

Investigation of a proactive glass filler removal in IC substrate build up films and its effect on topography and copper adhesion reliability

Stefan Kempa, Wolfgang Friz, Florian Gaul, Ellen Habig and Laurence J. Gregoriades
Atotech Deutschland GmbH,
Erasmusstraße 20,
10553 Berlin, Germany
Ph: +49-30-34985-223; Fax: +49-30-34985-618
Email: stefan.kempa@atotech.com

Abstract

In order to achieve interconnections at extremely small scale, the latest build up laminates contain increasing amounts of spherical glass fillers, which are needed to compensate the CTE mismatch between the epoxy based resin matrix and the electroplated copper circuits. Desmear of the resin surface during industrial processing exposes these glass fillers and weakens their anchoring in the surrounding resin matrix, which decreases adhesion strength of the plated copper.

We describe a newly developed cleaner process for the removal of glass fillers in industrially important build-up materials. Its effects on cleanliness and copper to resin adhesion is described in detail and illustrated by SEM imaging. Finally we propose a mechanism, explaining the adhesion increase as compared to standard processing and fluoride etch treatment.

Key words

cleaner, copper to resin adhesion, glass filler removal, IC substrates

I. Introduction

Facing a demand for increasing miniaturization, modern electronics manufacturers must pursue the trend to more and more densely interconnected multilayer printed circuit boards. Owing to their low cost and well-balanced physicochemical and mechanical properties, epoxy-based composites are insulating materials of prime choice [1] [2] [3]. The latest epoxy build up laminates contain increasing amounts of spherical glass fillers, which are needed to compensate the CTE mismatch between the epoxy based resin matrix and the electroplated copper circuits [4]. In addition, their small size in the order of μm and below, allows for smoother surface topographies compared to glass fiber bundle reinforced base materials.

Desmear of the resin surface during industrial processing exposes these glass fillers and weakens their anchoring in the surrounding resin matrix. If not removed, the remaining fillers may give rise to low adhesion of plated copper on the epoxy resin, as well as contaminated copper to copper connections in blind micro vias (BMVs) or through holes (TH), as shown in Fig. 1. This can affect yield rates in production and reliability in the final product.

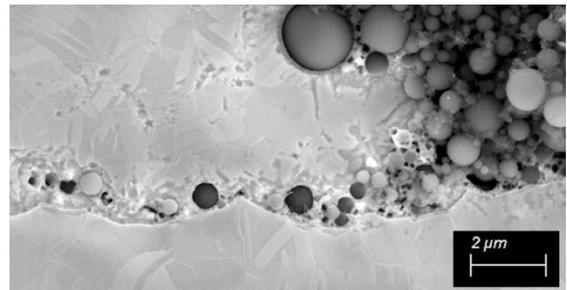


Fig. 1: Glass filler contamination in a BMV (lower side wall and capture pad), taken from a tear down of a current high end mobile phone.

Common approaches to overcome the glass filler contamination include fluoride etch solutions [5] and ultrasound treatment [6]. Neither of these strategies is easily applicable in the vertical mode of semi additive processing (SAP). The drastic health issues of fluoride etch solutions quickly disqualify them for most parts of the industry, whereas ultrasound application in vertical mode, possibly even in basket application, is extremely difficult to employ in a homogeneous fashion with sufficiently high impact on each panel.

In this paper we present a chemical approach to glass filler removal. We describe and discuss its effects on the surface topography and cleanliness prior to copper plating, as well as on the final copper adhesion on IC substrate build up films.

II. Materials and Methods

A. SAP base materials

The investigated epoxy base materials were Ajinomoto buildup films (ABF), acquired from Ajinomoto Fine-Techno Co., Inc. (AFT). Detailed names will be given where necessary. They were received as b-stage films by dry ice shipping and were stored at -18 °C in order to avoid any unwanted curing reactions. Film thicknesses ranged from 35 µm to 40 µm, and glass filler content varied between 42 and 74 wt%. The size of the embedded spherical glass fillers was an average of 0.5 µm in diameter, with a maximum of 5.0 µm.

B. Lamination and curing

The b-stage ABF were laminated onto Cu-cladded FR4 cores with roughened surfaces (BondFilm process, ATOTECH, Germany), using a vacuum laminator VA 7124-HP6 (Dynachem, Italy). For all ABF types the same lamination conditions were used (30 s vacuum time, 30 s dynamic slap-down time, 20 s static slap-down time, 2.0 mbar vacuum set-point, 5.0 kg/cm² pos. pressure).

Laminated panels were semi-cured in air-circulated ovens, using individual curing conditions for each material, according to supplier recommendations.

In-house laser drilling produced blind micro vias (BMVs) of 40 µm diameter, arranged in grids of 10 x 10 BMVs and 500 µm edge length. This layout readily allows investigation of BMVs, as well as surface area which remained unaffected by the heat dissipation during laser treatment.

After desmearing, PTH treatment, plating of e'less copper and electrolytic Cu (see section C), the panels received a final curing treatment (full-cure step), again using individual curing conditions for each material, according to supplier recommendations.

C. Desmear/PTH/e'less Cu/electr. Cu

For desmearing of the panels, PTH treatment and plating of electroless Cu, chemistry for SAP application was used in a vertical process according to datasheet set-points (Securiganth MV series, Neoganth MV series and Printoganth MV-TP1; ATOTECH, Germany).

Electrolytic copper was plated using the electrolyte Cupracid AC (ATOTECH, Germany) at 2 A/dm² surface area for 100 min, achieving a plated Cu thickness of ~40 µm.

D. Adhesion measurements

Adhesion strength of plated copper onto the epoxy base material was evaluated according to an internal test method, which is based on IPC-TM-650 number 2.4.8c [7]. E'less Cu was reinforced with electrolytic Cu as described above, to reach a final layer thickness of at least 35 µm. The coupons were cut into strips of 1 cm width, using a CNC supported milling machine. The forces required for peeling the Cu film on these strips off the epoxy support were measured using a material testing machine Unimat Plus 050-2kN (ERICHSEN GmbH & Co. KG, Germany), equipped with a 20 N load cell, at a peeling speed of 50.8 mm/min, ensuring a peeling angle of 90° at all times. The presented values are usually averages of 8 measurements distributed on two coupons from two repetitions.

E. Roughness measurements

Surface roughness of ABF films was evaluated using an interference microscope MIC-250 (ATOS GmbH, Germany). For each sample, the surface was imaged on 5 measuring windows of 124.8 µm × 124.8 µm. From these values the average roughness (S_A) and the relative surface area increase (RSAI) were calculated.

F. SEM investigations

Surface topography of the ABF specimens was investigated in detail using a field emission scanning electron microscope (FESEM) Sigma 500 VP (CARL ZEISS Microscopy GmbH, Germany), equipped with a secondary electron (SE) detector under high vacuum. The samples were sputtered with iridium at a tilt angle of 30° and measured at the same tilt angle.

III. RESULTS AND DISCUSSION

The presented studies concentrated on the direct comparison of an established cleaner process (process 1) and a newly developed alkaline cleaner process, with a specially designed surfactant system for glass filler removal on IC substrates (process 2). The performance of each process was judged by detailed topography elucidation on the base material surface and in the BMVs (via scanning electron microscopy - SEM), SEM investigation of cross sections, as well as adhesion measurements via peel strength tests. By way of example, most of the subsequent investigations will be shown for a single ABF material, the discussed results and trends being transferable to the other investigated ABF materials.

A. Glass Filler Removal

SEM samples for glass filler assessment were taken directly before and directly after e'less Cu plating. Fig. 2 shows the situation directly after desmear treatment (a), as compared to the situation after the cleaner processes 1 and 2. While cleaner 1 removes some of the excess glass fillers, many fillers remain visible (Fig. 2b). As can be seen in Fig.

2c, cleaner process 2 removes the majority of loose glass fillers, with almost all of the remaining fillers being considerably embedded in the resin matrix.

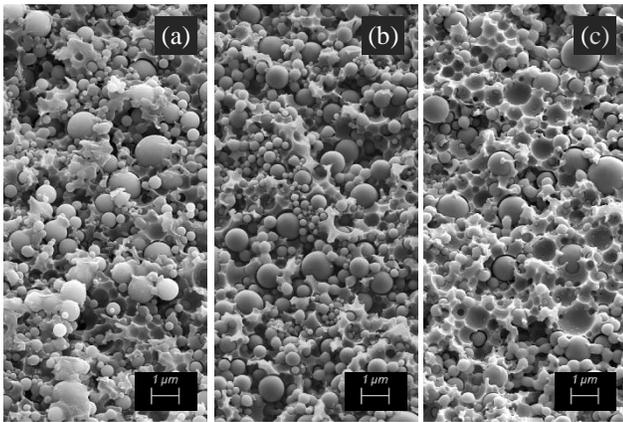


Fig. 2: Glass filler assessment on the surface of GX-T31R directly before e'less Cu plating (SEM, 5kx), (a) after desmear, (b) after process 1, (c) after process 2.

The positive effect on glass filler removal by cleaner process 2 is even more pronounced when monitored in the 40 μm BMVs. Again, cleaner 1 reduces the amount of glass fillers left after the desmear treatment, but fails to remove all (cp. Fig. 3a and b). In contrast, cleaner 2 removes the vast majority of loose glass fillers, leaving a clean hole wall and a clean capture pad (Fig. 3c). This performance is supported by the dedicated surfactant system adjusting the surface tension of the cleaner 2 solution, thus making it more penetrating into small features like the investigated BMVs. As well, the surfactant system promotes dispersion of the released glass fillers, which facilitates glass filler transport from the base material surface into the bulk cleaner solution.

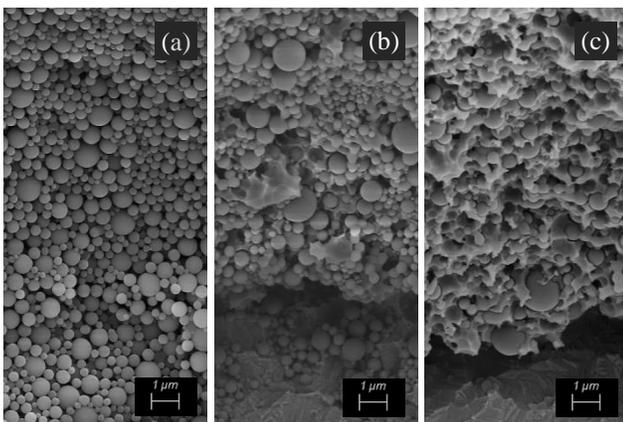


Fig. 3: Glass filler assessment in the BMV (2/3 hole wall, 1/3 capture pad) of GX-T31R directly before e'less Cu plating (SEM, 5kx), (a) after desmear, (b) after process 1, (c) after process 2.

In cross section investigations of BMVs after e'less Cu plating, the different amounts of remaining glass fillers

often perish in the general surface roughness. Nevertheless, Fig. 4 gives an example in which the greater amount of glass fillers after cleaner 1 treatment (a) shows as additional surface roughness, especially in the BMV, as compared to the cleaner 2 treated sample (b).

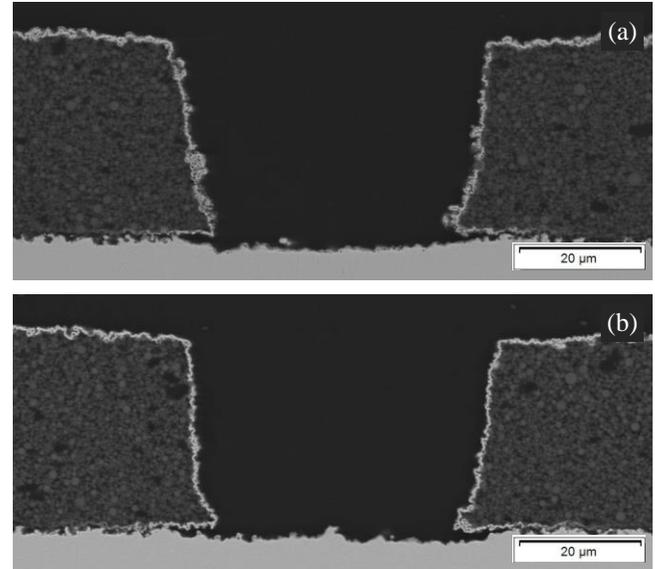


Fig. 4: Cross section investigation of the glass filler removal performance on GX-T31R after e'less Cu plating (SEM, 1kx), (a) after process 1, (b) after process 2.

B. Adhesion investigation

One of the most desired benefits of cleaning the desmeared ABF surfaces from loose glass fillers is an increase of adhesion of the plated copper to the underlying epoxy matrix. An obvious reason for anticipating this adhesion increase would be to assume an insufficient bonding of 'loose' glass fillers to the substrate. This should be the case for fillers that are less than half embedded in the surrounding epoxy resin after desmear or for any reabsorbed fillers. Copper is then plated around these fillers and upon exertion of peeling force, they are easily lifted from the substrate.

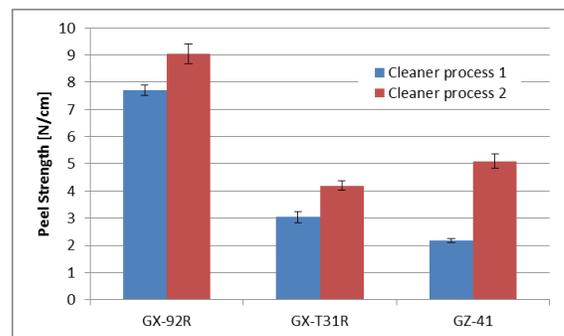


Fig. 5: Adhesion performance of cleaners 1 and 2, investigated by peel strength experiments on different base materials.

In peel strength experiments we have investigated this supposed increase in copper to resin adhesion and indeed we have found that using the cleaner process 2 gives significantly higher adhesion values (Fig. 5). One needs to keep in mind that the absolute adhesion values are strongly dependent on the exact topography, which in turn is ruled by the previously applied curing and desmear conditions [8] [9]. Besides, we have found a much improved blister performance on a variety of different base materials.

Table 1: Average surface roughness S_A and relative surface area increase RSAI of the ABFs investigated in Fig. 5.

S_A [nm]	GX-92R	GX-T31R	GZ-41	BU material #4
before cleaner	330 ± 20	275 ± 7	150 ± 10	184 ± 5
cleaner process 1	309 ± 3	272 ± 8	167 ± 9	178 ± 4
cleaner process 2	310 ± 10	260 ± 40	154 ± 10	167 ± 3

RSAI [%]	GX-92R	GX-T31R	GZ-41	BU material #4
before cleaner	53 ± 4	56 ± 1	26 ± 4	43 ± 2
cleaner process 1	63 ± 1	52 ± 5	38 ± 3	42 ± 2
cleaner process 2	61 ± 2	50 ± 10	31 ± 4	39 ± 1

Usually one finds a tight correlation of adhesion performance to the surface roughness of a given base material. Interestingly, in the presented investigations the observed high adhesion results are not accompanied by correspondingly higher surface roughness values (cp. Table 1).

C. Adhesion mechanism – Anchoring points

As described above, we observed an adhesion improvement without the expected increase in surface roughness. In order to cope with this apparent contradiction one might want to bear in mind that roughness evaluation is always a tradeoff between high resolution for catching small details and low resolution for just enough averaging on non-homogeneous surfaces. In detailed SEM studies we have found indications that go along these lines and show the creation of nano- and micrometer scale structures that could act as additional anchoring points, without significantly increasing the observed roughness (e.g. Fig. 6).

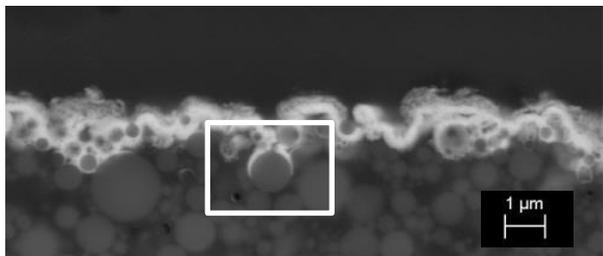


Fig. 6: Cross section detail of the surface topography on GX-T31R after e-less Cu plating (SEM, 5kx), an example for additional anchoring by wedge formation being highlighted.

In order to elucidate how these fine features are being created, investigations on very smooth base materials are obviously more helpful than on relatively rough materials.

For this purpose, we have chosen to only mildly desmear the epoxy resin AFT GX-92. As can be seen in Fig. 7a, the untreated surface is very smooth, exhibiting a small number of nm-sized cave-ins, which most likely originate from near surface outgassing during the curing process. Very few of the visible glass fillers are surface exposed (e.g. top left). After exposition only to a very mild desmear treatment (Fig. 7b), the surface appearance barely shows any changes. Minimal erosion of the resin matrix leads to somewhat more exposed glass fillers at the surface. If the mild desmear is complemented by a mild glass etching treatment, we observe circular gaps around the glass fillers, as shown in Fig. 7c. The creation of these gaps by glass etching rather than resin attack is supported by weight loss experiments. While the cleaner process 2 gives significant weight loss values on strongly desmeared base materials (many glass fillers exposed), we could hardly detect any weight loss on non-desmeared base material (close to zero exposed glass fillers). After filling the described crevices with plated copper, they may act as additional anchoring points, in analogy to the situation shown in Fig. 6, and cause the significant increase in adhesion strength.

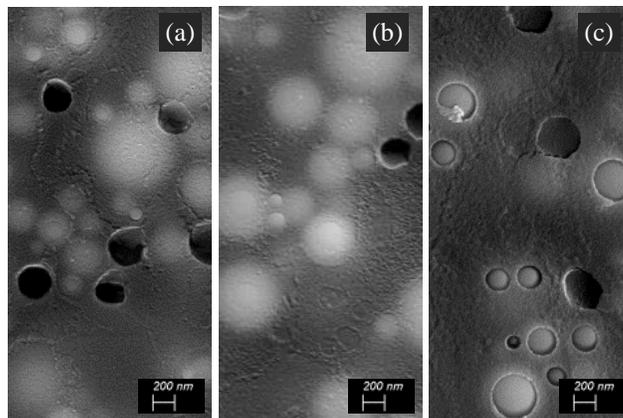


Fig. 7: Surface topography details on GX-92 (SEM, 20kx) (a) Untreated surface, (b) after short desmear, (c) after short desmear + mild glass etching treatment.

Combining all the different investigation results we propose the mechanism of adhesion increase as shown in Fig. 8. While the left-hand pathway shows the standard process with copper being plated on top of the exposed glass fillers, the right-hand path adds glass filler removal treatment. By this extra treatment, sufficiently loose glass fillers are dispersed into the cleaner solution with the help of the cleaner's surfactant system. At the same time the tightly bound, but surface exposed glass fillers are etched by the cleaner, creating additional anchoring points and thus increasing adhesion.

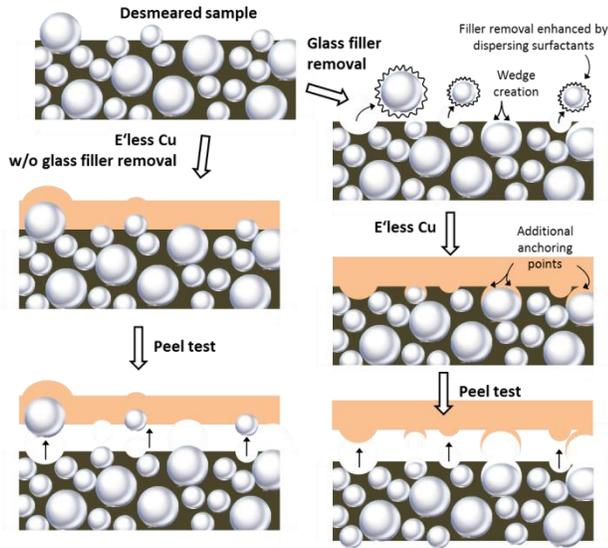


Fig. 8: Proposed mechanism of the adhesion increase by glass filler removal and soft glass etching.

Interestingly, in our hands excessive glass etching as is observed with fluoride containing etchants was counterproductive. Complete dissolution of all accessible glass fillers gave unstable sponge like structures of the epoxy base material, which in the end resulted in cohesive failure inside of the bulk matrix.

IV. Conclusion

In the light of increasing amounts of spherical glass fillers being added to SAP base materials, we have described the characteristics of a newly developed proactive glass filler removal process. Detailed SEM investigations have shown the superior cleaning properties compared to a standard process. Nearly all of the desmear exposed loose glass fillers are being removed, creating clean surfaces and BMVs. We observed that a suitable surfactant mixture can change the solution exchange properties into these features in such a way that the glass filler removal therein is optimized. It seems obvious to expect higher yield rates and better reliability after adopting this improved cleaner process e.g. for multilayer build-ups of printed circuit boards.

Examinations of adhesion properties on industrially relevant IC substrate base materials have shown significantly higher peel strength values after treatment with the new process. For example we have observed up to 9 N/cm on AFT GX-92R and an excellent 5 N/cm @ 154 ± 10 nm average surface roughness (S_A) on the generally challenging AFT GZ-41. In addition, the new process also improves the blister performance on a wide variety of very smooth base materials. It must be noted that the absolute values of peel strength certainly depend on the actual surface topography, which in turn is strongly ruled by the

curing conditions of the base material and the applied desmear process.

Finally we have proposed a mechanism that explains the increased copper to substrate adhesion when a mildly etching attack on the glass fillers is employed (as compared to e.g. fluoride containing etchants). Less residual glass fillers on the surface offer fewer possibilities to be easily lifted off by the plated Cu-film. Additionally, crevices are being created between the remaining surface exposed glass fillers and their surrounding resin matrix. After being filled during copper plating, these crevices act as additional anchoring points, increasing the overall adhesion between copper and base material.

Acknowledgment

We thank Senguel Karasahin for kindly providing the tear down picture in chapter I and Matthias Dammasch for laser drilling the ABF test coupons.

References

- [1] F.-L. Jin, X. Li and S.-J. Park, "Synthesis and application of epoxy resins: A review," *J. Ind. Eng. Chem.*, vol. 29, pp. 1-11, 2015.
- [2] D. Manassis, L. Boettcher, A. Ostmann, R. Aschenbrenner and H. Reichl, "Innovative Approaches for Realisation of Embedded Chip Packages - Technological Challenges and Achievements," in *Proc. - Electron. Components Technol. Conf.*, 2009.
- [3] M. Tani, S. Sasaki and K. Uenishi, "Adhesion Improvement on Smooth Cu Wiring Surfaces of Printed Circuit Boards," *Trans. Jap. Inst. Elec. Pack.*, vol. 4, no. 1, p. 24-30, 2011.
- [4] M. Goosey and M. Poole, "An introduction to high performance laminates and the importance of using optimised chemical processes in PCB fabrication," *Circuit World*, vol. 30, no. 4, pp. 34-39, 2004.
- [5] S.-C. Kwon and S.-M. Lee, "Circuit board and manufacturing the same". United States Patent US2012/0298109A1, 2012.
- [6] Y. Asahi and Y. Yukiiri, "Method for cleaning surface of resin layer". United States Patent US2007/0131243A1, 2007.
- [7] "Peel strength of metallic clad laminates," *IPC-TM-650 2.4.8c*, 1994.
- [8] S. Siau, A. Vervaet, A. Van Calster and D. Baert, "Development of epoxy polymer surface roughness due to wet chemical treatments and its relevance to adhesion of electrochemically-deposited copper," *Adhesion Aspects of Thin Films*, vol. 3, p. 1-20, 2007.
- [9] S. Siau, A. Vervaet, L. Van Vaeck, E. Schacht, U. Demeter and A. Van Calster, "Adhesion Strength of the

Epoxy Polymer/Copper Interface for Use in
Microelectronics," *J. Electrochem. Soc.*, vol. 152, no. 6,
pp. C442-C455, 2005.