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EcoFlash™: Next Level of Enhanced Isotropic Etchants

F. Michalik, N. Luetzow, G. Schmidt, T. Huelsmann, M. Kloppisch, R. Haidar, P. Brooks

Atotech Deutschland GmbH
10553 Berlin, Germany
Fabian.Michalik@Atotech.com, Rami.haidar@atotech.com

ABSTRACT

With the trend towards miniaturization IC-manufacturers are permanently requested to increase the density of interconnects generating conductors featuring finer lines and spaces. Advanced manufacturing technologies such as *Semi-Additive-Processing* (SAP) and *advanced Modified-Semi-Additive-Processing* (aMSAP) were devised, realized and implemented in order to meet the requirements.[i] According to the roadmaps of the major Original Equipment Manufacturers, line and space requirements of copper conductors become increasingly finer and will be below 5/5µm for the future packaging substrates.[ii]

SAP as well as aMSAP processes are based on pattern plating the desired circuitry on a thin conductive copper seed layer and finalizing the circuit formation afterwards by removal of the respective seed layer using so called flash/differential etching solutions.

Herein we report about the performance of the new developed ferric sulfate based EcoFlash™ process for SAP and aMSAP application with the focus on performance and fine line capability in comparison with hydrogen peroxide etchants.

INTRODUCTION

Commonly used differential etchants are based on sulfuric acid / hydrogen peroxide in combination with different organic additives. Main advantage of this etchant type is the uniform and fluid independent etch attack. However these etchants own several drawbacks. On the one hand the process has to run in feed & bleed mode to maintain a stable copper content and replenish the consumed oxidizer. Hence considerable amounts of chemical waste are being generated and thereby require cost-intensive waste treatment. On the other hand this etchant type is well known to form undercut of the conductor tracks (up to several micrometer), which is clearly affecting the mechanical stability and hence interfacial integrity especially for fine line conductors (track width < 10 µm).

As an alternative etching solution and complete new concept a recyclable ferric sulfate based process was introduced to the market by Atotech.[iii] The etching solution was based on oxidation of solid copper by iron(III).

Etching

$$Cu^0 + 2\,Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$$

Regeneration

$$\text{Anode:}\quad Fe^{2+} \rightarrow Fe^{3+} + e^-$$

$$\text{Cathode:}\quad Cu^{2+} + 2e^- \rightarrow Cu^0$$

Figure 1: Etching Mechanism

A unique benefit of this ferric sulfate based concept is the possibility to regenerate the consumed oxidizer (iron(III)) in an electrolytic cell at the anode. Besides the regeneration of the oxidizing agent the etched copper will also be removed from the solution by plating solid copper at the cathode.

A ferric sulfate based differential etching solution shows several advantages. Firstly this type of etchant does not exhibit undercut as obtained for the peroxide based process of record (POR). A second advantage is the fact that by utilization of an electrolytic regeneration unit the process becomes nearly waste water free. No feed & bleed operation is required to maintain constant bath parameters in contrast to the POR, with a big impact on the overall process costs. The small dosing required is mainly governed by the drag-out loss. In addition the etched copper is reclaimed on-site as pure copper and can be used to the economic benefit of the customer. Based on the described first-generation product and in order to maintain the cost (recyclable, less waste water), and functional advantages (no undercut formation) and to further improve the performance of ferric sulfate based etching solutions EcoFlash™ was developed.

PROCESS PERFORMANCE

Main drawback of most none-peroxide based etching solutions is the fluid dependent etching characteristics. Highly agitated areas are etched faster than slowly agitated ones. We implemented the Rotating Disk Electrode (RDE) as a tool to simulate etchant agitation influences in a well-controlled environment and to provide highly accurate and precise results.[iv]

The RDE-measurements inducing a laminar solution flow across the surface and form a diffusion layer between the electrode surface and the bulk of the evaluated solution. The thickness of the respective diffusion layer can be directly controlled as a function of rotation velocity (in rounds per minute, rpm). Increased rotation speed increases laminar flow of solution over the electrode surface, reducing the thickness of the diffusion layer and vice versa.

It enables different “ideal” flow conditions by controlling the diffusion layer thickness and hence the rotation-velocity.[v] To gain information about the influence of the EcoFlash™ additive package on the etching performance the ferric sulfate based etching solution with and without EcoFlash™ additives was compared against POR for different rotation speeds.

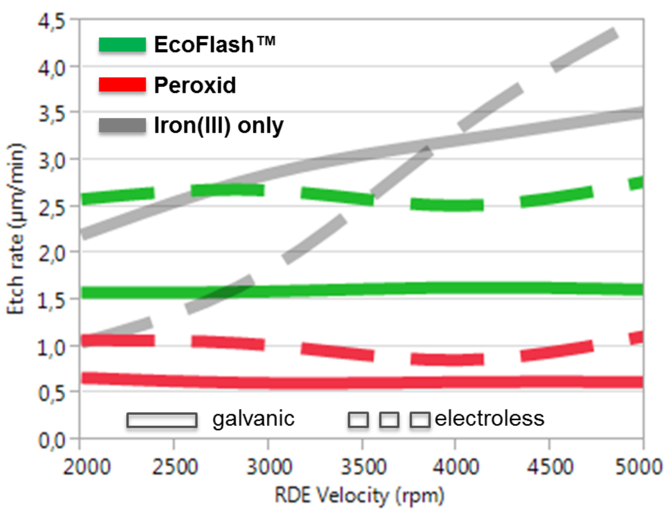

Figure 2: Results of RDE measurements for iron and peroxide based etchants

As expected the etch rate of peroxide etchants turned out to be completely independent on the solution agitation within the tested range. Over the whole agitation window the etching of electroless copper is slightly more favored over the galvanic copper. This is most likely connected to the smaller copper crystals in the electroless layer and hence a faster intergranular etch attack.
In contrast to the peroxide based etchant the additive free iron(III)-based etching solution is highly affected by the solution agitation. Also strong differentiation regarding the copper crystal structure can be found as well for the additive free system.

By adding the EcoFlash™ additive package to the iron(III) etchant it’s performance dramatically changed. The etch rate becomes completely independent of the rotation speed and hence the solution agitation. Also the ratio between electroless and galvanic copper remained constant (slightly higher etch rates for electroless copper).
Meaning, the mass transport of the iron(III) to the surface is uniform controlled by the EcoFlash™ additive and hence an even etching distribution over the whole surface can be achieved.

To prove this agitation independent characteristics of EcoFlash™ etch rates were evaluated for different spray pressures and compared to an additive free iron(III) etchant in a normal spray tool.

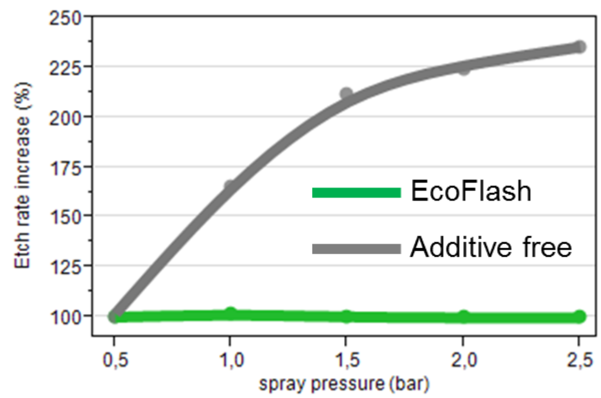

Figure 3: Etch rate changes with increased spray pressure

It could be confirmed that the additive package developed for EcoFlash™ is able to change the intrinsic solution characteristics and mimic the behavior of peroxide etchant. Thus, EcoFlash™ performance is independent on solution agitation to the benefit of uniform etch distribution regardless the line and space requirements.

Additionally EcoFlash™ fulfills all performance criteria of IC-substrate manufacturers. The process offers minimized etching on the conductor tracks (minimized line width reduction) combined with a fast and complete seed layer removal. SEM images of conductors (L/S = 15/15 µm) partially protected during EcoFlash™ process allow a direct comparison between unetched and etched areas on the same conductor.

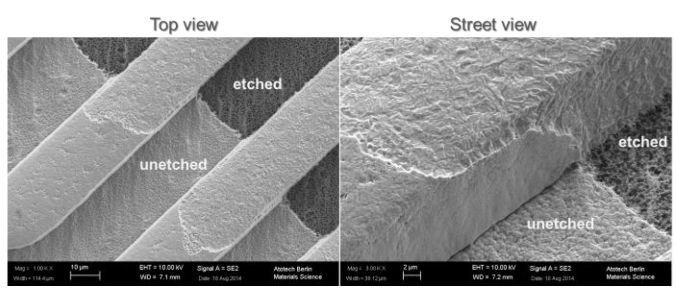

Figure 4: SEM images of SAP-conductors partially etched with EcoFlash™

The SEM images show minimal line width reduction during the process (etched depth = 1.8 µm), confirm a uniform performance along/across the conductor sidewalls and illustrate excellent shape of the conductors after processing. The roughness of the conductors is only slightly affected by the process. Finally no over-etching of the copper on the interface dielectric material/ conductor appeared.

The performance of EcoFlash™ was further evaluated by comparison against conventional hydrogen peroxide based etchants. For this purpose fine line SAP (L/S = 10/10 µm) and aMSAP (L/S = 23/15 µm) samples were treated till complete seed layer removal.

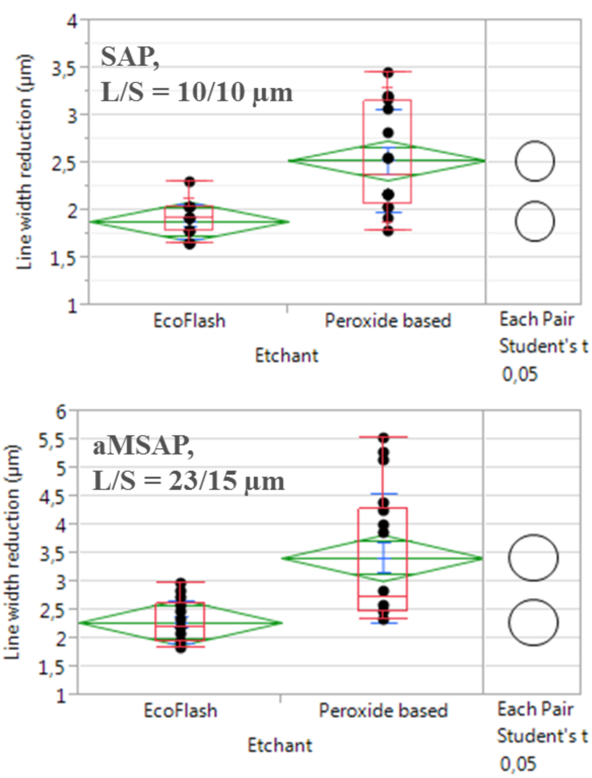

Figure 5: Line width reduction of EcoFlash™ compared to peroxide based system for SAP & aMSAP samples

In both cases EcoFlash™ resulted in significant lower line width reduction compared to peroxide based etchant. Noticeable is the strong variance of results for the peroxide based solution. It is caused by one of the major drawbacks of peroxide based etching solutions – undercut formation.

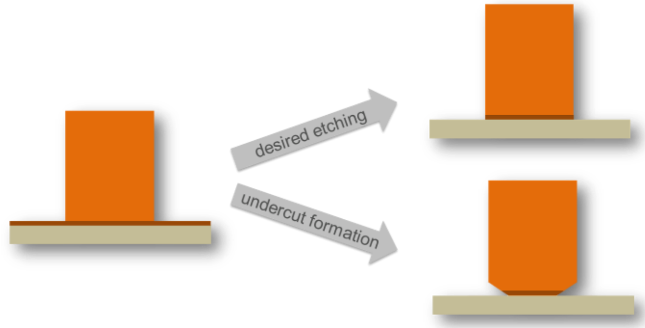

Figure 6: Schematic undercut formation

The undercut formation is not linear with the etch depth. Especially for higher etch depths it increases dramatically.

In production site, variation in seed layer thicknesses on a board will be overcome by increasing the overall etch depth for the differential etching process. This should ensure the complete removal of the seed layer.

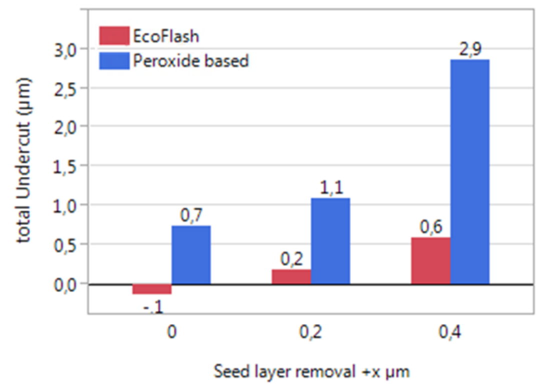

Figure 7: Undercut occurrence while over-etching

This kind of over-etching significantly pronounces the undercut formation for hydrogen peroxide based systems, whereas for EcoFlash™ the undercut remained on a negligible level. In contrast to the POR, EcoFlash™ allows a complete removal of the seed layer while ensuring the interfacial integrity and mechanical stability of the conductors.

The peroxide induced undercut formation can be a severe roadblock for the fine line capability. An acceptable undercut of 1 µm for 15 µm conductors correlate to ~13 % adhesion loss, whereas the same undercut resulted in 40% adhesion loss when dealing with 5 µm conductors.

By processing very fine conductors (≤ 5 µm) the advantage of EcoFlash™ against the POR is obvious.

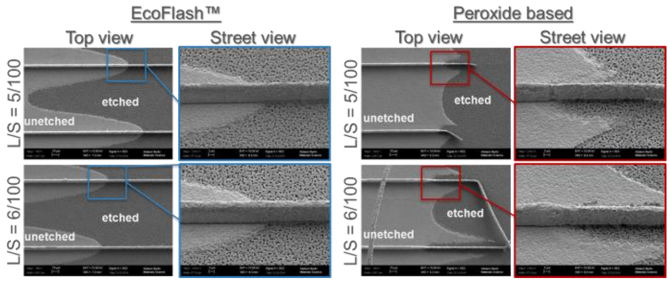

Figure 8: Comparison between EcoFlash™ and peroxide based etchants for fine lines.

Peroxide based etchant resulted in undercut formation which leads to a separation between conductor and dielectric material due to adhesion loss. Furthermore a severe line width reduction will be obtained. In contrast EcoFlash™ kept the interfacial integrity while the seed layer is completely removed. After processing the bare conductors adhere on the dielectric material and only minimal line width reduction can be observed. Furthermore the line width reduction is independent of the conductor size which proves the concept of uniform etch attack.

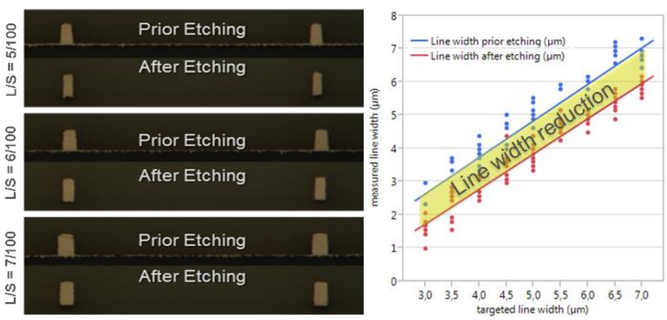

Figure 9: Fine line cross section and line width reduction examples prior/after EcoFlash™.

The constant etching performance (minimized line width reduction, no undercut formation) even for conductors down to minimal line and spaces is one of the key advantages of EcoFlash™ and ensure the differential etching capability for the future packaging substrates.

Regeneration Unit

To maintain a constant copper content while using conventional hydrogen peroxide based differential etching systems a certain amount of chemistry has to be removed continuously (bleed) and replenished by copper free working solution (feed). The bleed is fully functional chemistry that has to be wasted, which increases chemical costs for the process and additionally for the waste water treatment. For a typical hydrogen peroxide etchant for SAP application 500ml/m2 have to be bled, resulting in daily 500 to 1000 l of fully functional chemistry to be wasted.

In contrast to the feed & bleed operation the ferric sulfate based etchant will be maintained by delivering continuously solution from the etching module to a regeneration unit. At the inert anodes the regeneration of iron(III) occurs, while at the cathode copper is being plated, which can be sold as pure copper to recycling firms. After passing through the regeneration cell the regenerated etchant flows back to the etching chamber. The fact that no bleed is required to maintain the process performance reduces not only the process cost but also considerably the environmental footprint. In addition valuable pure copper is obtained further increasing the economic advantage of the regenerative etchant system.

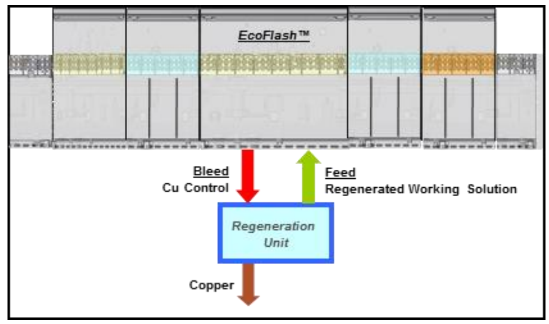

Figure 10: Schematic of the regeneration hook-up

To ensure high process stability the utilization of an online controller is mandatory. For this purpose a photometer device is being used to analyze the Fe^{3+} and Cu^{2+} content and to adjust the electrical current setting of the rectifier to ensure a consistent etching speed. In contrast to peroxide etchants, for the ferric etchant system all solution parameters are kept constant throughout the solution lifetime.

Although the regeneration concept was presented before, the module itself was re-designed to optimize functionality and reduce cost. The new design permits a flexible positioning of the regeneration unit anywhere on the shop floor and eliminating the need to place the unit directly next to the etching module. Optimization of the unit design increases the regeneration capacity thereby reducing the overall footprint. Previously higher demands for regeneration capacity required a complete new regeneration unit. The new design is flexible; extension modules can be added without the need to change the rectifier, the pumps or the electrical connection bus bars. Finally the handling of the anodes and solution storage was adapted to ensure a safe and easy usage and maintenance of the unit.

SUMMARY & CONCLUSION

By the trend towards miniaturization IC-manufacturers implemented advanced manufacturing processes like SAP and aMSAP. These techniques require a differential etching step to remove the copper seed layer. The current process of record employs hydrogen peroxide as oxidizer. Beside economical consideration (cost of waste water treatment, feed & bleed operation) one major drawback of this etchants is undercut formation and hence the maintaining of the interfacial integrity especially for fine line application.

Herein we reported about a new developed ferric sulfate based differential etching system named EcoFlash™. The additive packages within EcoFlash™ lead to agitation independent etch attack and ensure minimal line width reduction. In contrast to peroxide etchants no undercut occur even with prolonged etching. This enables fine capability and optimized etching results even for small conductors (5µm).

Furthermore the ferric sulfate based EcoFlash™ process is operated with a recovery unit which offers the possibility to regenerate the solution in by-pass equipment and therefore eliminating the need for feed & bleed operation. This concept greatly reduces the amount of copper contaminated waste water and hence process costs. Besides regenerating the oxidizer pure copper is plated, which can either be re-used internally or sold to recyclers. EcoFlash™ as a new differential etching process is in line with Atotech's global commitment to reduce the environmental footprint associated with clear economic benefits in day to day operation.

[i] Nishiwaki et al., Part I & II, PCB 007, 2010
[ii] Nishiwaki et al., Part II, PCB 007, 2010
[iii] Luetzow et al., IMPACT, 2012, pp. 230 - 233
[iv] Potts et al., *paper in preparation*
[v] A. J. Bard, L. R. Faulkner, "Electrochemical Methods: Fundamentals and Applications", 2nd Ed., John Wiley & Sons, New York, 2001, pp. 335-360