CupraEtch FH™: New advanced low-etch depth soldermask and photoresist pretreatment

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ABSTRACT

One key application for the manufacturing of MLB and HDI printed circuit boards are pretreatment systems aimed at providing the optimum adhesion of organic coatings such as Photoimagable Resists (such as Dry Films [DF] and Liquid Photo Imageable Resists [LPIR]) or Solder Mask's (SM). The most common way for this optimum adhesion to be achieved is to use an etching solution to roughen the copper surface to give the highest possible increase in surface area with the minimum removal of copper.

Probably the most challenging of these applications is the adhesion promotion for SM. This is because the improvement in adhesion here must be on a "permanent" basis as once the SM is applied, the good adhesion of the SM to the copper surface must continue through the life of the panel through all downstream processes. This includes application of final solderable finishes such as Immersion Tin and ENIG (both of which can damage the SM integrity and can attack the SM to Copper interface) and throughout final assembly where repeated high temperature soldering applications must be withstood.

The industry demand for finer lines and spaces, higher signal integrity and above all lower etch depth requirements for the above described DF, LPIR and SM pretreatments have to be balanced with the performance demands for the application in question the OEM performance demands to the final panel.

In this regard, Atotech here present a new ferric-sulfate based process CupraEtch FH^{TM} which is both technically and commercially superior to existing POR pretreatment chemistries.

INTRODUCTION

Commonly used etchants are based on sulfuric acid / hydrogen peroxide or on $CuCl_2$ in combination with different organic additives. Main advantage of these etchant types is the relative low initial cost. However these etchants have several drawbacks. On the one hand, these processes are running with big feed/bleed volumes to maintain a stable copper concentration, which clearly impacts in the final cost. They also generate considerable amounts of chemical waste and thereby require cost-intensive waste treatment. This again bears a cost for the PCB manufacturing and also has considerable environmental impacts. On the other hand, these etchants, especially H_2O_2/H_2SO_4, often exhibit low organic additive stability, which normally means higher dosing amounts and shorter bath lifetimes. This again adds to the cost in use. Also they present some limitations regarding the equipment used during their application, for $CuCl_2$ only Titanium and for H_2O_2 only Stainless steel metal parts, which clearly narrow down the flexibility of these systems.

PROCESS DESCRIPTION

As an alternative etching solution and complete new concept a ferric sulfate based process is introduced to the market by Atotech. The etching solution is based on oxidation of solid copper by iron(III). Because it is based on ferric sulfate, the CupraEtch FH^{TM} system is applicable to any spray modules equipped with Titanum and/or Stainless steel metal parts. But this added flexibility is only one of the several advantages this new system presents.

Other of its key advantages is the simplicity of the system: the CupraEtch FH^{TM} process only involves two steps: cleaning and etching as it is shown in Figure 1. No further steps like post dips are required, neither to remove residues nor to condition the surface prior to soldermask treatment.

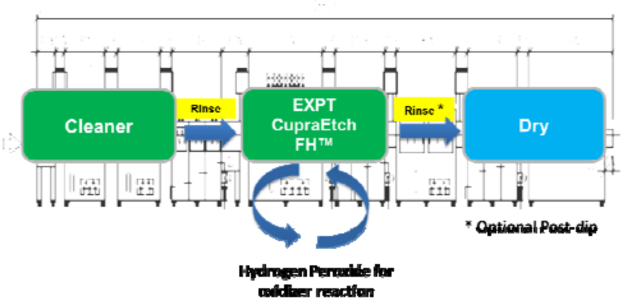

Figure 1: Schematic for the process

Another asset of CupraEtch FH^{TM} system is the high stability the additives exhibit in this iron-based system, especially in comparison to the traditional POR systems using peroxide, where the standard decomposition rates for the organic components are very high. These high performance additives guarantee a much longer life bath, no issues with idle time and the complete absence of sludge, which clearly reduce the running cost for the process. One extra advantage coming from the high stability of the additives is that the bath can hold without any issue a high copper loading, up to 60 g/L Cu. This high copper bath loading together with the ultra-low etch depth (see more details in this regard below) allow the system to be run with small feed/bleed conditions, in the range of the drag-out, which are around four times smaller than those required for the $CuCl_2$ and sulfuric acid / hydrogen peroxide systems. All these advantages of the CupraEtch FH™ certainly reduce the running cost for the process and also minimize the waste water.

The clean chemical regeneration of the etchant is another clear advantage of the CupraEtch FH™ process. The simple addition of hydrogen peroxide, together with sulfuric acid, permits the fast re-oxidation of Fe(II) to Fe(III) as it can be seen in the scheme below. This chemical regeneration is taking place immediately which avoids the formation of any undesired side products that might affect the performance and stability of the working bath. This Fe(III) regeneration procedure can be easily controlled and adjusted to the different requirements of the PCB manufacturer.

Etching process

$$Cu + Fe(III) \rightarrow Cu(II) + Fe(II)$$

Regeneration process

$$2\,Fe(II) + H_2O_2 + 2H^+ \rightarrow 2Fe(III) + 2\,H_2O$$

Surface Morphology

Apart from the different advantages already described for the process, there is distinct characteristic from the CupraEtch FH™ that stands out over the rest: the very unique surface morphology. For this system, the singular additive combination creates very deep trenches in the copper surface that ensure an extraordinary adhesion to the resist. These trenches are located mainly at copper grains and there homogenously distributed all over the surface. As an example they can be easily seen in the Figure 2 for a sample with an etch depth of 0,5 µm. In the FE-SEM image, a cavernous, brain-like structure can be clearly observed. However, to get a deep look to the unique morphology of the CupraEtch FH™, a FIB cut is required as shown in below (Figure 2). For the case exposed here (ED 0,5 µm) the trenches exhibit values around one micron.

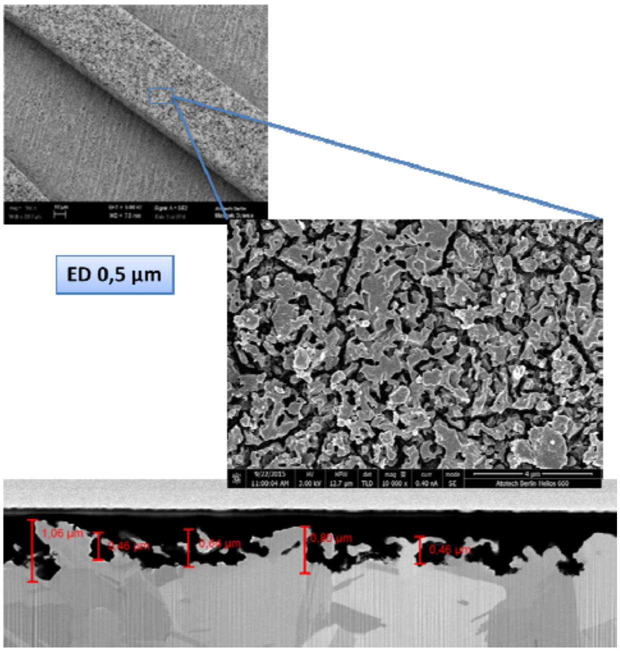

Figure 2: FE-SEM and FIB cut for a sample with ED 0,5 µm

The depth of trenches present on the CupraEtch FH™ surface depend on the etch depth. The higher the etch depth, the deeper it is the nature of these characteristic features. For samples with different etch depths, from 0,2 to 0,7 µm, the mean roughness depth (Rz) was measured and represented together with the respective FIB cuts in Figure 3. The relationship between the Rz and the etch depth is almost linear indicating that, within this range, the more it is etched, the more profound are the trenches.

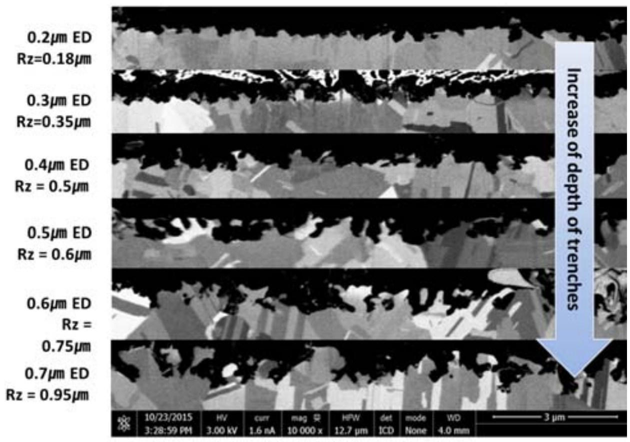

Figure 3: FIB cuts for CupraEtch FH™ with different etch depths

Process Performance

The presence of this characteristic copper surface morphology implies an outstanding adhesion of the copper to the soldermask. In the Table 1 it is summary for the adhesion performance test by standard tape test (IPC TM 650 2.4.1.E) after immersion Tin and ENIG when using the soldermask

Taiyo PSR 4000 G23K and Atotech's internal test artwork for Soldermask. For benchmarking, the results for a competitive $CuCl_2$ pretreatment system have been also included. In the case of ENIG, even with such low etch depths as 0,2 µm no peeling was observed for developed Soldermask features down to 10µm. For the Immersion Tin process, an etch depth of 0,5 µm is sufficient for CupraEtch FH^{TM} to match the results obtained by the POR system but in that case with an ED 1,3 µm. This excellent adhesion for ultra-low etch depths is a straightforward outcome of its unique surface, where the deep trenches described previously play a key role. The ultra-low etch depths together with its high copper loading allow the process to have a very low bleed within the range of the drag-out, which signicantly reduces the running cost for the process and reduces waste water volumes.

Taiyo PSR-4000 G23K	Items	Competitive $CuCl_2$ system	CupraEtch FH						
	Etch depth	1.3um	0.2um	0.3um	0.4um	0.5um	0.6um	0.7um	0.8um
	Etchrate	1.3um/min	1.2um/min						
	Line Pattern Tape test after FC	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	ENIG & Tape test	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	Imm. Tin & Tape test	>30um	>80um	>50um	>40um	>30um	>30um	>20um	>20um

Taiyo PSR-4000 G23K	Items	M (CuCl2 system)	CupraEtch FH						
	Etch depth	1.3um	0.2um	0.3um	0.4um	0.5um	0.6um	0.7um	0.8um
	Etchrate	1.3um/min	1.2um/min						
	Line Pattern Tape test after FC	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	ENIG & Tape test	>10um	>10um	>10um	>10um	>10um	>10um	>10um	>10um
	Imm. Tin & Tape test	>30um	>80um	>50um	>40um	>30um	>30um	>20um	>20um

Table 1: Summary of the CupraEtch FH^{TM} performance with soldermask

To get a better understanding why the difference in the performance for the CupraEtch FH^{TM} and the other systems is so sizable, a look to the FIB cuts for samples with different etch depth can offer a good overview (Figure 4). In these case, three different etch depths (0,5, 0,8 and 1,3 µm) for CupraEtch FH^{TM} and for competitive $CuCl_2$ were selected. It can be seen that the outline of the copper surface for the 0,5 µm CupraEtch FH^{TM} is much more pronounced that the one present for 1,3 µm competitive $CuCl_2$, which can clearly explain the contrast between the performance of both processes.

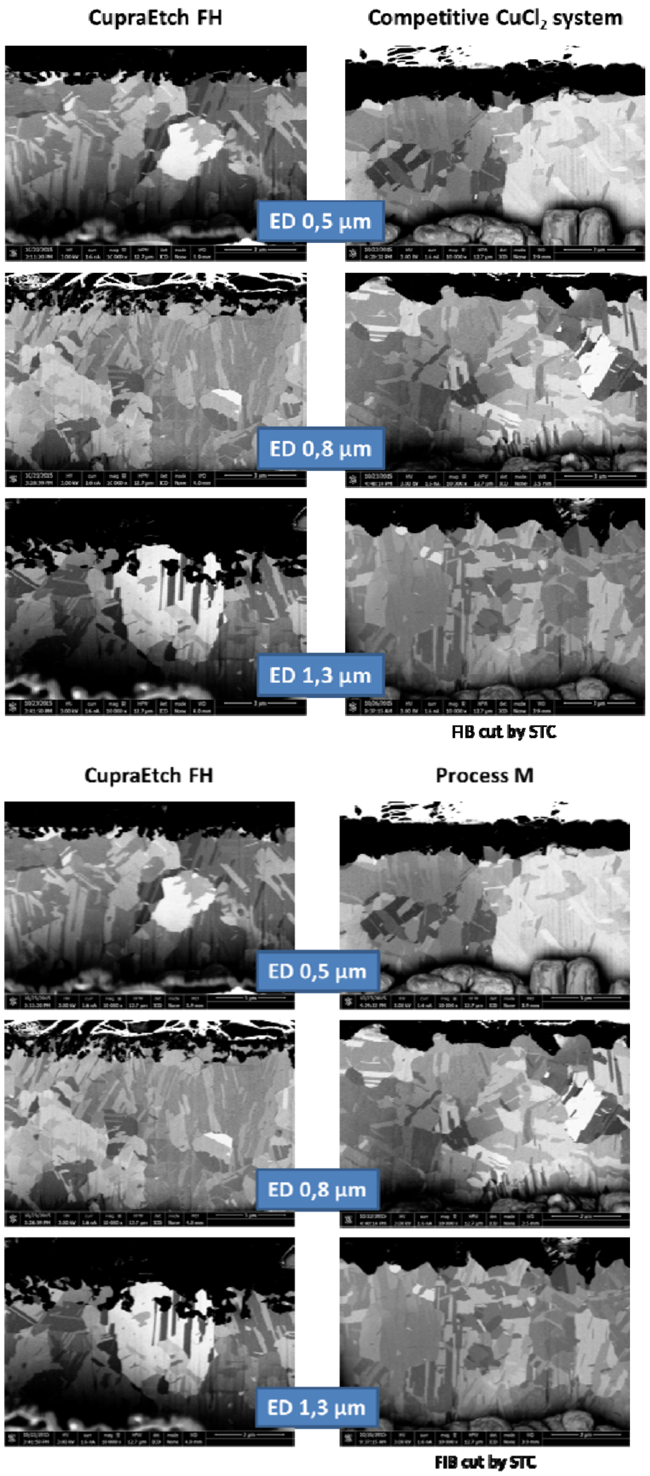

Figure 4: FIB cut with different etch depths for CupraEtch FH^{TM} and $CuCl_2$ base etchant (M)

Conclusions

- On the whole, CupraEtch FH^{TM}, developed by Atotech, is a new ferric-based in which the additives exhibit a high stability These high performance additives guarantee a much longer life bath , high copper loading of the bath (up to 60 g/L Cu), no issues with idle time and the complete absence of sludge.

- The clean chemical regeneration of the etchant is another clear advantage. The simple addition of hydrogen peroxide, together with sulfuric acid, permits the fast re-oxidation of Fe(II) to Fe(III) without any undesired side products.

- The CupraEtch FH™ creates very deep trenches in the copper surface that ensure an extraordinary adhesion to the resist. These trenches are mainly at copper grains and their size depends on the etch depth: for example, when an etch depth of 0.5 µm is applied, the length of these trenches is around 1 µm.

- The presence of this characteristic copper surface morphology implies an outstanding adhesion of the copper to the SM even for low etch depth like 0.5 µm. This excellent adhesion for ultra-low etch depth together with its high copper loading provide another important advantage for CupraEtch FH™, because they allow the process to have low bleed within the range of the drag-out, which signicantly reduces the running cost for the process and reduces waste water volumes.